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APPLIED COLLOID CHEMISTRY

GENERAL THEORY

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APPLIED COLLOID CHEMISTRY

GENERAL THEORY

BY

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PREFACE

The earlier books on colloid chemistry presented the subject empirically because no other method was then possible. While we do not now know much about gelatinous precipitates and jellies, the theory of the rest of the subject is in fairly good shape and consequently I have written this book deductively. While my point of view differs considerably from Freundlich's, it is a pleasure to acknowledge my debt to him for what he did in his admirable book.

This volume on general theory should be followed by at least one volume on each of the following subjects: silicate industries; paints and varnishes; plastics; fibers and dyeing; photochemistry and photography; petroleum industries; ore flotation and allied subjects; foods and beverages; soils and crops; biology and medicine. Allowing a minimum of three years to a volume, it seems very improbable that I shall write all of these single-handed. With the general theory of the subject once cleared up, there is no reason why the other volumes should not be written by people whose knowledge of the special subjects is much greater than my own.

I am indebted to Messrs. Bray, Briggs, Clowes, Holmes, Johnston and Lamb for reading the manuscript and for critical comments on it.

Cornell University,
November 1, 1920.

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APPLIED COLLOID CHEMISTRY

INTRODUCTION

In 1861 Graham[1] pointed out that substances like potassium hydroxide, potassium sulphate, magnesium sulphate, sugar, and alcohol diffuse much more rapidly in water than hydrous silicic acid, hydrous alumina, starch, dextrin, the gums, albumin, tannin, gelatine, etc. Since these latter substances occur usually in a non-crystalline or even gelatinous form, Graham suggested calling them colloids from the French word for glue. Substances which diffused rapidly were to be called crystalloids because many of them crystallized readily. Graham believed that the distinction between a crystalloid and a colloid was fundamental and was due to some molecular condition. Though modern colloid chemistry begins with Graham,[2] his distinction between crystalloids and colloids has been dropped. A colloidal substance is not necessarily amorphous, for colloidal gold is certainly crystalline at times and possibly always. We now speak of a colloidal state instead of a colloidal substance, and we call any phase colloidal when it is sufficiently finely divided or dispersed,[3] without committing ourselves definitely as to what degree of subdivision is necessary in any particular case. The subdivided phase is often called the internal or dispersed phase and the enveloping phase the external phase or the dispersing phase. In fog the rain drops are the dispersed phase and the air the dispersing phase, while the solid particles are the internal phase in the case of smoke. When a milky liquid is obtained by precipitating barium sulphate in the cold, the barium sulphate is the dispersed

[1] Phil. Trans. **151,** 183 (1861); Jour. Chem. Soc., **15,** 216 (1862); **17,** 318 (1864).

[2] Interesting work was done by Selmi in 1844; but it had no appreciable effect on the development of scientific thought.

[3] Cf. Wolfgang Ostwald: Grundriss der Kolloidchemie, 79 (1909).

phase and the solution the dispersing phase. In emulsions of oil in water, the oil is the internal phase because it is present in drops. When benzene is emulsified to a solid jelly in a small amount of soap and water, we have a mobile liquid as dispersed phase in a viscous mass. Bread or Ivory soap might be considered as a system with air as internal phase, and a fairly solid external phase. In a porous plate or a fine sponge the two phases are, or may be, continuous and it is therefore better to classify these as interlacing systems. True ruby glass consists of gold as dispersed phase in glass as a non-crystalline dispersing phase. With salt colored by exposure to cathode rays, we have metallic sodium as internal phase in an external phase of crystalline sodium chloride.

Adopting the very flexible definition that a phase is called colloidal when it is sufficiently finely divided, colloid chemistry is the chemistry of bubbles, drops, grains, filaments, and films, because in each of these cases at least one dimension of the phase is very small. This is not a truly scientific classification because a bubble has a film round it and a film may be considered as made up of coalescing drops or grains. It is a convenient classification, however for many purposes. At first sight colloid chemistry may not seem to be an important branch of chemistry, either theoretically or technically; but this opinion changes when we consider that a knowledge of colloid chemistry is essential to anybody who really wishes to understand about: cement, bricks, pottery, porcelain, glass, enamels; oils, greases, soaps, candles; glue, starch, and adhesives; paints, varnishes, lacquers; rubber, celluloid, and other plastics; leather, paper, textiles; filaments, casts, pencils, and crayons; inks; roads, foundry cores, coke, asphalt; graphites, patines; zinc, phosphorus, sodium, and aluminum; contact sulphuric acid, hardened oils, etc.; beer, ale, and wine; cream, butter, cheese, and caseine products; cooking, washing, dyeing, printing; ore flotation, water purification, sewage disposal; smoke prevention; photography; wireless telegraphy; illuminants; comets; pharmacy; physiology. In other words, colloid chemistry is the chemistry of every-day life.

CHAPTER I

ADSORPTION OF GAS OR VAPOR BY SOLID

Adsorption of Gas or Vapor by Solid

In an extremely subdivided phase, the surface is very large relatively to the mass of the phase and it is therefore advisable to discuss the properties of surfaces, beginning with the behavior of solids in contact with gases or vapors. All solids tend to adsorb, or condense upon their surface, any gases or vapors with which they are in contact. The amount of adsorption for given conditions of pressure and temperature varies with the nature and physical state of the solid and with the nature of the gas; in other words, the adsorption is specific or selective. With the same solid and the same gas the amount of adsorption is greater the higher the pressure of the gas and the lower the temperature. Hunter[1] showed that many different gases and vapors are adsorbed by charcoal to a marked extent. While his experiments are probably not very accurate, and are not made at strictly comparable temperatures and pressures, they cover more ground than those of anybody else. Some of his data are given in Table I. In Table II are some data by Dewar[2] with cocoanut charcoal at low temperatures. The volumes of gas adsorbed have been calculated back to standard conditions; in other words to the volumes which the adsorbed gases would occupy at 0° and 760 mm pressure. Thus at −185° and 760 mm the actual volumes of gas adsorbed would be only 88/273, or approximately one-third, of the values given in Table II. This correction was not applied by Hunter in his work.

[1] Phil. Mag. (4) **25,** 364 (1863); Jour. Chem. Soc., **18,** 285 (1865); **20,** 160, (1867); **21,** 186 (1868); **23,** 73 (1870); **24,** 76 (1871); **25,** 649 (1872).

[2] Proc. Roy. Soc., **74,** 124 (1904).

TABLE I.—ADSORPTION OF GASES AND VAPORS BY COCOANUT CHARCOAL

Volumes gas adsorbed per volume charcoal.
Temperature in Celsius degrees.
Pressures in millimeters of mercury.

Gas	Vol.	Temp.	Press.	Gas	Vol.	Temp.	Press.
Acetic acid	83	159	676	Acetaldehyde	67	155	687
Water	24	159	24	Acetaldehyde	139	100	681
Water	44	128	624	Ammonia	22	127	655
Benzene	59	130	646	Ammonia	83	70	760
Ethyl alcohol	84	160	663	Ammonia	88	60	760
Ethyl alcohol	111	127	644	Ammonia	96	50	760
Ethyl alcohol	141	100	652	Ammonia	114	40	760
Ethyl acetate	72	154	659	Ammonia	149	20	760
Carbon tetrachloride	4	155	695	Ammonia	176	0	760
Carbon tetrachloride	8	100	636	Cyanogen	87	70	760
Methyl alcohol	61	159	684	Cyanogen	92	60	760
Methyl alcohol	127	129	663	Cyanogen	96	50	760
Methyl alcohol	151	100	652	Cyanogen	99	40	760
Chloroform	21	159	660	Cyanogen	107	20	760
Chloroform	30	100	651	Cyanogen	114	0	760
Acetone	68	157	671	Hydrochloric acid	60	100	668
Acetone	105	100	642	Nitrous oxide	64	100	661
Carbon bisulphide	91	158	659	Carbon dioxide	17	127	687
Carbon bisulphide	117	100	671	Carbon dioxide	71	0	760
Ethyl ether	54	160	684	Nitrogen	15	3	760
Ethyl ether	68	128	661	Hydrogen	4	3	760
Ethyl ether	87	100	644				

TABLE II.—ADSORPTION OF GASES BY COCOANUT CHARCOAL

Volumes gas adsorbed per volume charcoal.
Pressures not given; volumes corrected to 0° and 760 mm.
Temperature in Celsius degrees.

Gas	Vol.	Temp.	Gas	Vol.	Temp.
Argon	12	0	Nitrogen	15	0
Argon	175	−185	Nitrogen	155	−185
Oxygen	18	0	Hydrogen	4	0
Oxygen	230	−185	Hydrogen	135	−185
Carbon monoxide	21	0	Helium	2	0
Carbon monoxide	190	−185	Helium	15	−185

In Table III are given some more recent data by Hempel and Vater,[1] who used a special animal charcoal, which they mixed to

[1] Zeit. Elektrochemie, **18**, 724 (1912).

a stiff paste with ox-blood diluted tenfold with water and which they then charred at 600°.

TABLE III.—ADSORPTION OF GASES BY SYNTHETIC CHARCOAL

Volumes gas adsorbed per volume synthetic 600° charcoal.
Volumes probably corrected to 0° and 760 mm.

	+20°	−78°	−185°		+20°
H_2	7.3	19.5	284.7	H_2S	213.0
N_2	21.0	107.4	632.2	Cl_2	304.5
CO	26.8	139.4	697.0	NH_3	197.0
O_2	25.4	122.4		SO_2	337.8
	+20°	−78°		+20°	−78°
Ar	12.6	92.6	CH_4	41.7	174.3
NO	103.6	231.3	C_2H_4	139.2	360.7
N_2O	109.4	330.1	C_2H_6	119.1	275.5
CO_2	83.8	568.4	C_2H_2	135.8	488.5

TABLE IV.—BOILING-POINTS OF VARIOUS LIQUIDS

Liquid	B. Pt.	Liquid	B. Pt.	Liquid	B. Pt.
He	−268.7	C_2H_6	−84	CH_3CHO	+20.8
H_2	−252.6	HCl	−82.9	$(C_2H_5)_2O$	+34.6
N_2	−195.7	C_2H_2	−82.4[1]	CS_2	+46.2
CO	−190.	CO_2	−79[1]	Br_2	+58.6
Ar	−186.1	H_2S	−60.2	$CHCl_3$	+61.2
O_2	−182.8	Cl_2	−33.7	CH_3OH	+64.7
CH_4	−164.	NH_3	−33.5	CCl_4	+76.7
NO	−153.	$(CN)_2$	−21.	C_2H_5OH	+78.4
C_2H_4	−105.	SO_2	−10.	C_6H_6	+80.2
N_2O	− 89.8			H_2O	+100.0

For purposes of reference there are given in Table IV the boiling-points of some of the substances whose adsorption by carbon has been studied. As a first approximation it is often stated that a gas or vapor is adsorbed more readily the higher its boiling-point. Thus helium is taken up by charcoal much less than hydrogen, and hydrogen again is adsorbed to a much less extent

[1] Sublimation point.

than nitrogen or oxygen. Carbon dioxide is adsorbed less readily than ammonia, so that these substances follow the empirical rule. Argon, however, is adsorbed less completely by charcoal than is nitrogen, while carbon monoxide is adsorbed to a greater extent at 0° than either argon or oxygen, though according to the rule this ought not to be so. Nitrous oxide is adsorbed less strongly than ethylene, and nitric oxide more strongly than methane, which is not according to the boiling-points. Ethane, ethylene, and acetylene are adsorbed more at +20° than is carbon dioxide, though the last is the most readily condensible gas of the four. The difference between carbon dioxide and hydrogen sulphide is in the right direction; but seems out of all proportion to the difference in boiling-points. Hydrogen sulphide is adsorbed more than ammonia, which is wrong; and chlorine is adsorbed much more strongly than ammonia, although the two boiling-points are practically identical. Cyanogen is adsorbed more than ammonia at 70° and less at 0°. In the case of vapors there is no relation between boiling-point and adsorption. Going from higher to lower boiling-points, we have the order: water, benzene, ethyl alcohol, carbon tetrachloride, methyl alcohol, chloroform, ether, and aldehyde. The order from greater to lesser adsorption is methyl alcohol, ethyl alcohol, aldehyde, ether, benzene, water, chloroform, and carbon tetrachloride. The truth of the matter is that adsorption is specific and varies with the nature of the gas and of the adsorbing solid. One charcoal is not like another. In Table V are Hunter's results on charcoal

TABLE V.—ADSORPTION OF GASES BY CHARCOAL FROM DIFFERENT WOODS

Volumes gas adsorbed per volume charcoal.
Temperature = 0°C; pressure = 760 mm.

Wood	Vol. NH_3	Vol. CO_2	Vol. $(CN)_2$	Wood	Vol. NH_3	Vol. CO_2	Vol. $(CN)_2$
Logwood	111	55	87	Jamaica logwood	69	33	
Ebony	107	47	90	Sapan wood	70	32	
Camwood	91	45		Beech	58		
Green ebony	90	41		Rosewood	51		
Fustic (Cuba)	90	58		Wistaria sinensis	44		
Lignum vitæ	89	47		Vegetable ivory	...	50	57
Boxwood	86	31	29	Cocoanut shell	176	71	114

made from different woods. The cocoanut charcoal has the greatest adsorbing power of all and, of the others, logwood charcoal has the greatest adsorbing action on ammonia, fustic charcoal on carbon dioxide, and ebony charcoal on cyanogen. It is not the most porous charcoal in the ordinary sense which adsorbs the most gas, because Hunter says that the charcoal made from the shell of the cocoanut is very dense and brittle. The pores are quite invisible and, when the charcoal is broken, the fracture presents a semi-metallic lustre. It has been suggested by De Saussure[1] that charcoals with very many pores of very small diameter are the best adsorbers because they present the largest surfaces for condensation. This is not quite right because there are other factors besides the extent of surface, among them the arrangement of the surfaces. A plane surface will adsorb a given amount of a gas under standard conditions, but two plane surfaces placed close to each other will apparently adsorb a good deal more gas than the same surfaces would if each did not re-enforce the other and modify the concentration gradient. The adsorption depends not only on the surface but on the structure of the the adsorbing material. Narrow pores, down to a certain limit, should adsorb more than spherical pores of large diameter and this actually happens. Table VI shows the change in the adsorption of air[2] when different charcoals are heated from $-100°$ to $+500°$. In a number of cases the parallelism between density and adsorption holds but by no means in all cases. While there may be an actual difference in the amount of surface, we are undoubtedly dealing with another factor, the presence in the charcoal of substances which affect the adsorption. Charcoal is far from being pure carbon and the great improvements in charcoal as used in warfare have been along the line of cleaning the charcoal very thoroughly in addition to increasing the surface. While cocoanut charcoal is usually considered the best, the sour cherry charcoal in Table VI does better; and the synthetic charcoal of Hempel and Vater[3] was better than the best cocoanut charcoal which could then be obtained, though far inferior to the best cocoanut charcoal of today. The varying

[1] Cf. Dewar: Proc. Roy. Inst., **18,** 180 (1905).
[2] Piutti and Maglia: Gazz. chim. ital., **40** I, 569 (1910).
[3] Zeit. Elektrochemie, **18,** 724 (1912).

behavior of charcoal from cocoanut shell, logwood, fustic, and ebony is probably due to the presence of different impurities which affect different gases in different ways.

TABLE VI.—BEHAVIOR OF DIFFERENT CHARCOALS

		Apparent density	cc gas per cc charcoal −100° to +550°	
			Air	Cl_2
Prunus cerasus	Sour cherry[1]	1.6393	280.1	312.7
Cocus nucifera	Cocoanut[1]	1.4497	251.8	334.2
Phillyrea media	Jasmine box	1.4970	222.4	260.0
Grevillea robusta	Silk oak	1.4383	212.7	
Abies alba	White spruce	1.1901	199.5	
Castanea vesca	European chestnut	1.3000	186.3	
Buxus sempervirens	Common box	1.4192	138.5	
Liospunos kaki	Chinese persimmon	1.3398	134.5	
Populus nigra	Black poplar	1.2802	134.1	
Prunus virginiana	Choke-cherry	1.2359	133.0	
Ceratonia siliqua	Carob[1]	1.6274	131.5	
Prunus armeniaca	Apricot[1]	1.3994	129.5	
Juglans regia	English walnut	1.3132	118.6	
Pinus rigida	Pitch-pine	1.3114	111.1	
Robinia pseudo-acacia	Common locust	1.2218	99.9	

Charcoal is used in most gas masks, because it is the best all-round adsorbent for toxic gases.[2] The removal of the toxic materials must be surprisingly complete. The adsorbent must be capable of reducing the concentration of the toxic gas from, say 1000 p.p.m.[3] to 1 p.p.m. or less within the 0.1 second that the air takes in passing through the canister. This is accomplished with a safe margin by the present gas mask materials. In fact it has been shown that charcoal will reduce a concentration of 7000 p.p.m. of chloropicrin, CCl_3NO_2, in a rapidly moving current of air to less than 0.5 p.p.m. in something under 0.3 seconds.

Some use has been made in peace times of the fact that properly

[1] Shells and kernels.

[2] LAMB, WILSON and CHANEY: Jour. Ind. Eng. Chem., **11**, 420 (1919).

[3] Parts per million by volume.

prepared charcoal will adsorb gases to a considerable extent. Melsens[1] placed wood charcoal, saturated with dry chlorine, in the longer branch of a bent sealed tube and dipped that end of the tube into boiling water, while the shorter branch was placed in a freezing mixture. A portion of the gas was volatilized and the pressure thus developed caused liquefied chlorine to appear in the cold portion of the tube. Sulphur dioxide, hydrogen sulphide, hydrobromic acid, and cyanogen can be liquefied in the same way; but not bromine, hydrochloric acid, carbon bisulphide, ether, or alcohol.

In 1874 Tait and Dewar[2] described the use of charcoal as a means of getting a high vacuum. They placed a piece of charcoal in a tube having platinum electrodes, heated the tube to a red heat, exhausted it with a Sprengel pump and sealed it. If the tube was cool, no spark would pass when using an induction coil capable of giving a quarter of an inch spark. On heating the tube slightly some gas was given off from the charcoal and the spark passed. By making use of the increased adsorption at low temperatures quite surprising results were obtained.[3] A bulb of 300 cc capacity, containing air at 15° and an initial pressure of 1.7 mm, was connected with another bulb holding five grams of charcoal. When the charcoal was cooled in liquid air, the pressure dropped to 0.00005 mm. A Crookes radiometer tube, filled with hydrogen at atmospheric pressure, had a charcoal bulb attached. On dipping the charcoal bulb into liquid air, no rotation took place even when the beam from an electric arc was focussed on the vanes. The motion became quite rapid however when the charcoal bulb was placed in liquid hydrogen because the adsorption of hydrogen by charcoal is sufficient at these very low temperatures, though not at the temperature of liquid air. The adsorption of helium by charcoal at −252° is not enough to make this experiment successful when the radiometer tube is filled with helium.

Since different gases are adsorbed in different amounts, the ratio of two gases in the charcoal will differ from the ratio in the gas phase and a separation will be possible to some extent.

[1] Comptes rendus, **77,** 781 (1873); Jour. Chem. Soc., **27,** 120 (1874).
[2] Proc. Roy. Soc. Edin., **8,** 348, 628 (1874).
[3] Dewar: Proc. Roy. Inst., **18,** 437, 756 (1906).

Dewar[1] heated about 50 grams of charcoal and then saturated it at −185° in a current of pure dry air at atmospheric pressure, at 76 mm, and at 5 mm. The vessel containing the charcoal was taken out of the liquid air and the temperature allowed to rise to 15°. The volumes of gas given off were 5.7, 4.8, and 4.5 liters respectively and the oxygen concentration varied irregularly between 56 and 58 percent. These experiments show the practical constancy of the mean composition of the gases adsorbed by the charcoal under the conditions of these experiments and they therefore show that wide changes in the pressure of the air current have but slight effect in altering the relative proportions of the adsorbed gases. In another experiment the vessel containing the saturated charcoal was placed in a vacuum vessel containing a little liquid air so that the temperature might rise slowly. This made it possible to collect and analyze separately the successive liters of gas as evolved. The data are given in Table VII. The mean composition of the six liters was 56 per-

Table VII.—Distillation of Air Adsorbed by Charcoal

First liter	18.5 percent O_2	Fourth liter	72.0 percent O_2
Second liter	20.6 percent O_2	Fifth liter	79.0 percent O_2
Third liter	53.0 percent O_2	Sixth liter	84.0 percent O_2

cent oxygen. A few experiments were also made with special mixtures of nitrogen and oxygen. When a gas mixture containing 6.5 percent oxygen was used and the charcoal was heated rapidly to 15°, five liters of gas were obtained, containing 23 percent oxygen.

At higher temperatures the results seem to be quite different, though this may be due to the removal of oxygen by combustion. Skey[2] found that red-hot charcoal retains over three volumes of nitrogen which is given off when the cooled charcoal is immersed in water. Storey and Lewis[3] state that it is difficult to remove adsorbed nitrogen and carbon dioxide from coke even by heating

[1] Proc. Roy. Soc., **74**, 126 (1904); Proc. Roy. Inst., **18**, 184 (1905).
[2] Chem. News, **15**, 15, 27 (1867).
[3] Am. Chem. Jour., **4**, 409 (1883).

the containing flask to 200° and exhausting with a Sprengel pump. In these two cases the oxygen was probably burned completely. It is not so easy, however, to account for Blumtritt's results.[1] He heated various forms of charcoal under mercury to 140° in a paraffin bath and analyzed the gases which were given off. With common wood-charcoal the gas was pure nitrogen. After the same charcoal had been moistened and dried, the evolved gas contained 85.6 percent N_2, 2.1 percent O_2, 9.2 percent CO_2, and 3.1 percent CO. The gas from poplar charcoal consisted of 83.5 percent N_2, and 16.5 percent CO_2, that from crushed alder charcoal had the composition 78.9 percent N_2 and 21.1 percent CO_2, while charcoal made from ash yielded a gas consisting of 76.0 percent N_2, 9.1 percent CO_2, and 14.9 percent O_2. These variations, if real, probably depend on the nature and amount of the hydrocarbons left in each charcoal; but the experiments should be repeated. Craig[2] heated a Jena flask filled with lignite coke to redness, closed the flask and analyzed the contents. The unadsorbed gas was nearly pure nitrogen and so was the adsorbed gas, which meant that the oxygen had oxidized some unspecified hydrocarbon without burning it to CO or CO_2.

In Dewar's experiments the oxygen adsorbed at −185° was apparently given off at −15° without any appreciable contamination with CO or CO_2. Calvert[3] observed no reaction at ordinary temperatures, when carefully purified pieces of boxwood charcoal were heated to redness and, while still red-hot, were introduced into a cylinder standing over mercury and containing a measured volume of oxygen. Passing through the mercury undoubtedly cooled the charcoal a great deal before it came in contact with the oxygen. By special experiments Calvert satisfied himself that no carbonic acid had been formed, or existed, in the cube of charcoal. Since the adsorbed oxygen oxidized ethyl alcohol to acetic acid, and ethylene to carbon dioxide and water, it is certain that there cannot have been a serious error in analysis, because such oxidations could not be caused by carbon monoxide or carbon dioxide.

[1] Jour. prakt. Chem., **98,** 418 (1886).
[2] Chem. News, **90,** 109 (1904).
[3] Jour. Chem. Soc., **20,** 293 (1867).

Quite different results were obtained by C. J. Baker[1] working with purified blood charcoal which was allowed to adsorb oxygen at $-15°$ and was then pumped out. On heating the tube to 100° seven volumes of CO_2 were obtained when moist oxygen was used, while no gas was given off when dry oxygen was used. In a check experiment it was shown that no carbon dioxide was formed when water vapor and carbon were heated to 100° in a sealed tube for a week. The question arose whether dry oxygen was adsorbed or whether it was held more firmly than moist oxygen. Practically no gas was given off up to 350°. At 450° a regular stream of gas was given off which consisted of 99 percent CO and 1 percent CO_2 in those cases where the drying had not been done so carefully. Intermediate values were found for intermediate degrees of drying. Rhead and Wheeler[2] do not confirm Baker's results though this may be because they did their experiments differently. Rhead and Wheeler treated purified carbon at some definite temperature, 200°, 300°, etc., with air, pumped out the air, and then heated the charcoal more or less rapidly to 1100° and analyzed the gas. With an initial temperature of 300° and rapid heating to 1100° the composition of the evolved gas was 11.3 percent CO_2 and 88.4 percent CO when dried air was used, and 15.4 percent CO_2 plus 84.4 percent CO when moist gas was used. When the initial temperature was 300°, the gas coming off between 300° and 400° was composed of 57.0 percent CO_2 and 42.4 percent CO; between 400° and 500° the composition was 41.6 percent CO_2 and 58.0 percent CO, dropping to 0.8 percent CO_2 and 98.7 percent CO for the gas drawn off between 800° and 1100°. Baker found 1 percent CO_2 and 99.0 percent CO at 450°; but his initial temperature was $-12°$. The two sets of experiments should be repeated so that we might know whether they are or are not contradictory. Neither Rhead and Wheeler nor Baker found any oxygen in the gas given off above 200°. By determining the oxidizing action at different temperatures of charcoal containing adsorbed oxygen, it should be possible to determine approximately at what temperature all the oxygen was converted into CO and CO_2. In spite of all the excellent work that has been done on the com-

[1] Jour. Chem. Soc., **51**, 249 (1887).
[2] Ibid., **103**, 461, 1210 (1913).

bustion of carbon, there is still a great deal that we do not know. Hulett has found that there is a slow reaction between oxygen and charcoal at ordinary temperatures, apparently the formation of a non-volatile oxide.

When one blows a slowly dying wood fire with the bellows, the fire will often start burning briskly again, in spite of the fact that the large influx of cooler air must tend to chill the embers and thus to put the fire out. Bacon[1] suggests that the dying embers are covered with an adsorbed film of carbon dioxide which is swept away to some extent by the draught from the bellows. When the fire is burning briskly, there is less carbon dioxide adsorbed at the higher temperature and the natural draught is sufficient to bring oxygen to the burning wood. Though this hypothesis has not been proved, it is rendered more probable by the experiments of Arndt and Schraube,[2] who found that even at a red heat carbon dioxide is adsorbed more strongly than carbon monoxide or nitrogen. Manville's fluctuations of the ignition point of charcoal[3] are probably due to hydrocarbons which had not been removed.

Ramsay[4] has availed himself of Dewar's method of using cooled cocoanut charcoal as an adsorbent for gases to determine the amounts of neon and helium in the air. At 100° the oxygen, argon, and nitrogen are taken out practically quantitatively while the adsorption of neon and helium is negligible. At −185° practically all of the neon is adsorbed and none of the helium. From his observations, Ramsay concludes that the concentration of neon in the air is about 0.00123 volume percent and that of helium about 0.00044 volume percent, while the amount of free hydrogen cannot be greater than one five-hundredth of the combined volumes of the neon and helium. At great elevations this changes completely, the gas with the lowest molecular weight concentrating in the higher regions. Alleman[5] gives some data for the estimated concentrations of hydrogen at different heights above sea-level, Table VIII.

[1] Jour. Phys. Chem., **17,** 768 (1913).
[2] Nernst Festschrift, 46 (1912).
[3] Jour. Chim. phys., **5,** 297 (1907).
[4] Proc. Roy. Soc., **76A,** 111 (1905); **80A,** 599 (1908).
[5] Jour. Franklin Inst., **185,** 161 (1918).

Table VIII.—Estimated Distribution of Hydrogen in the Atmosphere

Height in kilometers	Percent hydrogen	Height in kilometers	Percent hydrogen	Height in kilometers	Percent hydrogen
140	99.2	80	64.7	20	0.04
130	99.0	70	32.6	15	0.02
120	98.7	60	10.7	11	0.01
110	98.1	50	2.80	5	0.01
100	95.6	40	0.67		
90	88.3	30	0.16		

Dewar[1] has worked out a very effective lecture experiment, based on the selective adsorption by charcoal. A number of spectroscopic tubes, connected in series with a large U-tube containing charcoal are exhausted by cooling the charcoal until the electric discharge will barely pass. The charcoal tube is now placed in liquid air and a current of air is allowed to enter the system slowly, passing first through the charcoal tube which takes out the readily adsorbed gases such as oxygen, nitrogen, and argon, while helium, neon and hydrogen pass through. When the pressure in the first tube has risen sufficiently it begins to glow with the well-known rich orange hue of neon. In time the characteristic discharge of neon and helium appears in the other tubes. The sensitiveness of the neon tubes to induced electric oscillations from a coil of wire placed at right angles to the tube may be shown. Claude[2] points out that the remarkable luminosity of neon can be utilized for lighting purposes. One of the difficulties of the problem is the ease with which neon is masked by small quantities of certain other gases. It is not enough to introduce very pure neon into a tube with electrodes under suitable pressure in order to obtain an effectively luminous tube. This can be overcome by removing these other gases with cooled charcoal, when the beautiful orange luminescence of neon appears, and retains its brightness. The light is very rich in red rays and Claude considers it just the corrective required for the light of mercury vapor tubes.

[1] Proc. Roy. Inst., **18**, 444 (1906).
[2] Mon. Sci., **74**, 135; Jour. Franklin Inst., **171**, 624 (1911).

Krypton and xenon may be obtained from the air by means of cooled charcoal.[1] A current of air passes through a series of tubes immersed in liquid air for the purposes of purification, the last tube containing cotton wool in order to retain any dust of the solid, condensed impurities. This pure air is passed through a tube containing about 100 grams of charcoal for at least 24 hours. The charcoal tube is then removed and placed in solid carbonic acid, and the gas which is evolved is allowed to escape. The gas remaining in the charcoal at $-78°$ is driven off by heating and exhaustion, and all the carbon compounds and oxygen removed from it. The remaining gas, consisting of nitrogen, krypton, and xenon, is separated into its constituents by condensation and fractionation. Instead of passing a current of air over charcoal at $-183°$, a few hundred grams of charcoal may be covered with liquid air and the latter may be allowed to evaporate in a silvered vacuum vessel. The gases remaining in the charcoal can then be separated as before. In this way spectrum tubes of krypton and xenon may be readily prepared.

Rutherford[2] found that cocoanut charcoal adsorbs radio-active emanations. A slow current of air charged with the emanations of radium, thorium, or actinium is deprived of some or all of its emanation in the passage through a tube filled with cocoanut charcoal, and for this purpose the charcoal need only be at ordinary temperature. The complete withdrawal of the emanation only takes place when the air is passed very slowly through the charcoal; if the speed is increased, the amount of unadsorbed emanation increases also. In another experiment Rutherford found that if a tube containing less than a gram of charcoal is connected to a vessel containing the emanation from several milligrams of radium bromide, the charcoal will adsorb the emanation in time. If some powdered willemite be mixed with the charcoal, the gradual adsorption is shown by the increasing brilliancy of phosphorescence of the willemite. It is not necessary to heat or exhaust the charcoal previously; but if this is done the emanation is adsorbed more rapidly. The charcoal retains the emanation at ordinary temperature but the greater

[1] Valentiner and Schmidt: Sitzungsber. Akad. Wiss. Berlin, **1905**, 816; Dewar: Proc. Roy. Inst., **18**, 445 (1906).

[2] Nature, **74**, 634 (1906).

part of it is expelled by heating to a low red heat. Boyle[1] showed that cocoanut charcoal adsorbed thorium emanation the most and ordinary charcoal the least, while animal charcoal came in between the other two. The rate of adsorption increased very much when cocoanut charcoal was used at $-75.5°$ and only slightly in the case of wood charcoal. At 211° cocoanut charcoal begins to give off carbon dioxide; but it shows some power of adsorbing thorium emanation up almost to 300°. It is not possible for the charcoal to become saturated with thorium emanation as may happen with other gases, because the thorium emanation adsorbed by the charcoal is decaying at the rate of half-value in 54 seconds.

The general rule for mixtures of gases seems to be[2] that the more readily adsorbed gas displaces the other to some extent and is adsorbed to a greater relative amount than one would have predicted from experiments on the single gases. This cannot be universally true. Bergter[3] found that at pressures of 0.5 to 10 mm oxygen is adsorbed 30 to 40 times as strongly as nitrogen, and that at these pressures the presence of oxygen increases the amount of nitrogen adsorbed. With readily condensible gases, one may have one of the vapors helping to carry down the other. Cases of this sort have been studied by Hunter,[4] the most striking instance being water and ammonia. It seems probable that the adsorbed water dissolves or adsorbs ammonia thus increasing the amount of ammonia apparently held by the charcoal. It has been shown by E. E. Reid that the presence of traces of benzene or ether in charcoal will increase the service time against chloropicrin.

The data in Table IX are not tabulated as one would like to have them; but they do indicate that the presence of a second gas will cut down the adsorption of the first,[5] though such comparisons should be made at equal partial pressures. Passing one gas over charcoal which has adsorbed another gas should theo-

[1] Jour. Phys. Chem. **12**, 284 (1908); Phil. Mag. (6) **17**, 374 (1909). See also Satterly: Phil. Mag. (6) **16**, 584 (1908); **20**, 778 (1910); Porlezza and Morsi: Atti Accad. Lincei, **20** I, 932 (1911).

[2] Freundlich: Kapillarchemie, 99 (1909).

[3] Drude's Ann. **37**, 480 (1912).

[4] Jour. Chem. Soc. **23**, 73 (1870).

[5] Hempel and Vater: Zeit. Elektrochemie, **18**, 724 (1912).

retically cause complete displacement of the adsorbed gas; but it is evident that the effectiveness will be much greater if one displaces the slightly adsorbed gas by the readily adsorbed one rather than the other way round. It would be very interesting to determine an isotherm showing the relative amounts of two gases in the vapor phase and the charcoal phase when in equilibrium at constant pressure.

TABLE IX.—ADSORPTION OF MIXED GASES BY SYNTHETIC CHARCOAL

Mixed gases with 0.4 g synthetic 600° charcoal.
Could adsorb about 30 cc ethane.

cc H_2	cc C_2H_6	Percent C_2H_6	cc gas adsorbed	Percent gas adsorbed	Percent C_2H_6 unadsorbed
95.0	5.0	5	3.7	3.7	1.5
45.0	5.0	10	3.8	7.6	2.5
20.0	5.0	20	3.8	15.2	5.0
11.7	5.0	30	4.4	26.4	7.5
6.1	5.0	45	4.6	41.4	9.5

cc H_2	cc CH_4	cc gas adsorbed	cc H_2	cc C_2H_4	cc gas adsorbed
95.0	5.0	1.3	95.0	5.0	3.6
15.0	5.0	2.7	15.0	5.0	4.4
6.1	5.0	3.3	6.1	5.0	5.1
2.7	5.0	3.9	2.7	5.0	5.5

cc H_2	cc C_2H_2	cc gas adsorbed	cc N_2	cc C_2H_4	cc gas adsorbed
95.0	5.0	3.6	95.0	5.0	6.2
15.0	5.0	4.7	30.0	5.0	9.6
6.1	5.0	5.2	12.2	5.0	10.7
2.7	5.0	5.7	5.4	5.0	11.6

A curious case has been cited by Matwin.[1] Charcoal will take carbon bisulphide and carbonyl sulphide out of illuminating gas, one kilogram of charcoal cutting the sulphur content of ten cubic meters of gas to 2.92 grams. Porous charcoals are the best,

[1] Jour. Gasbeleuchtung, **52**, 602 (1909).

such as pine and linden. Bone-black takes up almost no carbon bisulphide, and cocoanut charcoal is said to be even less effective. This is very remarkable, because cocoanut charcoal adsorbs carbon bisulphide strongly. We must either assume that the illuminating gas cuts down the adsorption of carbon bisulphide very much or that there is an error in the statement. If carbon bisulphide and illuminating gas were adsorbed in the same ratio in which they occur in the mixture, there would be no apparent purification even though the actual adsorption were very large.[1] This point calls for more study.

The adsorption of gases by charcoal has been studied extensively, because charcoal adsorbs so many gases and adsorbs them so strongly. Experiments have also been made with many other solids—silica, alumina, glass, wool, rubber, celluloid, meerschaum, metals, soils, etc. The behavior of glass is important because of its use in the laboratory, Mülfarth[2] states that the adsorption decreases in the order: NH_3, SO_2, N_2O, C_2H_2. Kundt and Warburg[3] found that a small amount of water is retained obstinately by glass even when the pressure is reduced practically to zero. In order to remove this water the glass must be heated, in which case one is likely to cause changes in the glass, setting free water vapor and gases that were not adsorbed in any proper sense of the term.[4] On the other hand, the film of water which usually covers glass surfaces is due chiefly to alkali dissolved from the glass.[5] It is hard to tell whether the change in the vacuum of a Crookes' tube is due to adsorption of the gas by the glass or not. Swinton[6] found that the inner surfaces of these tubes are roughened perceptibly after being subjected to cathode ray bombardment. When these portions of the tube are heated strongly in a blow-pipe, they immediately become clouded, owing to the formation of minute spherical bubbles which average about 0.01 mm in diameter. The centers

[1] Cf. LEIGHTON: Jour. Phys. Chem., **20,** 32 (1916).

[2] Drude's Ann., **3,** 328 (1900).

[3] Wied. Ann., **24,** 327 (1884); cf. BUNSEN: Pogg. Ann., **156,** 201 (1875).

[4] SHERWOOD: Jour. Am. Chem. Soc., **40,** 1645; Phys. Rev. (2) **12,** 448 (1918).

[5] WARBURG and IHMORI: Wied. Ann., **27,** 481 (1886); IHMORI: Ibid., **31,** 1006 (1887).

[6] Proc. Roy. Soc., **79A,** 134 (1907).

of the bubbles are about 0.12 mm from the inner surface of the glass. The number of bubbles per square centimeter of glass was found to be about 625,000, or about 0.000133 cc of gas per square centimeter. The gas is mostly hydrogen and is given off when the glass is powdered. It is not known whether the bubbles are connected with the inner part of the tube by minute channels or not. If they are, this is a case of adsorption. If the bubbles are actually buried in the glass owing to the latter flowing round them, that is not adsorption.

L. J. Briggs[1] showed that finely divided quartz adsorbs water vapor, though not to the same extent as amorphous silica. About 9 mg water was adsorbed at 30° by 50 g quartz having an estimated surface of 20,000 cm^2 when the vapor pressure was 26.1 mm, about 4.5 mg when the vapor pressure was 19.6 mm, and about 0.5 mg when the vapor pressure was 0.2 mm. Cohnstaedt[2] states that the gas given off by aluminum electrodes in a Crookes' tube is water vapor and not hydrogen, as usually believed. He claims to prove that glass and aluminum surfaces will retain water even when heated to 500° or when dried over phosphorus pentoxide. It is the presence of a water film of varying thickness on a glass or other vessel which makes it necessary to keep the moisture constant if accurate weighings are to be made. Professor Morley once said that it was a mistake to believe that it is a difficult matter to dry a gas. That is a very simple thing to do; but the difficulty is to dry the vessel which holds the gas.

Drucker and Ullmann[3] showed that the adsorption of a vapor by the glass containing vessel causes only a negligible error in vapor-density determinations with ether, alcohol, benzene, and chloroform; but the error may amount to 2 percent with acetic acid at 80°. At higher temperatures the adsorption decreases and the error is considerably less. The adsorption of ammonia by solid ammonium hydrosulphide introduces a serious error in the equilibrium relations for ammonia and hydrogen sulphide.[4]

[1] Jour. Phys. Chem., **9,** 617 (1905).
[2] Drude's Ann., **38,** 223 (1912).
[3] Zeit. phys. Chem., **74,** 567 (1910).
[4] Magnusson: Jour. Phys. Chem., **11,** 21 (1907).

While most solids, even though porous, do not adsorb gases as much as charcoal, yet Dewar[1] reports that dry aluminum oxide shows a remarkable power of adsorbing air at low temperatures, one gram condensing some 70 cc at atmospheric pressure. The adsorption by alumina decreases very rapidly with decreasing pressure, and consequently alumina cannot be used as a means of obtaining high vacua. Meerschaum and silica behave somewhat like alumina. On the other hand, high vacua can be obtained by means of copper powder.[2] Carbon dioxide[3] and water vapor[4] are both adsorbed strongly by alumina. Platinum black may take up 100 volumes of hydrogen and palladium nearly up to 3000 volumes of hydrogen,[5] but it is not certain whether this hydrogen is all adsorbed or is partly dissolved. In gas analysis palladium, heated to 100°, is used to remove hydrogen. This is purely a question of rate because equilibrium is reached more rapidly at the higher temperatures. Paal and Hohenegger[6] report on the adsorption of acetylene by palladium. Platinum black will take up more than 800 volumes of oxygen; but it seems certain that some of the platinum has been oxidized.[7] Celluloid adsorbs carbon dioxide[8] and rubber apparently adsorbs[9] it and also other gases, though it is possible that we have true solution in the case of rubber. Wool[10] adsorbs both hydrochloric acid and ammonia gas. Rohland[11] reports that unsaturated compounds are adsorbed by clay and oxygenated compounds by the oxides of silicon, aluminum, iron and titanium.

If the film of condensed air on a small particle remains of the same thickness irrespective of the diameter of the particle or if it does not decrease too rapidly with decreasing diameter, the ratio of air film to mass of particle will increase as the particle

[1] Proc. Roy. Inst., **18,** 435 (1906).
[2] Merton: Jour. Chem. Soc., **105,** 645 (1905).
[3] Scheermesser: Centralblatt (3) **1,** 165 (1870).
[4] Johnson: Jour. Am. Chem. Soc., **34,** 911 (1912).
[5] Paal and Gerum: Ber. deutsch. chem. Ges., **41,** 805 (1908).
[6] Ber. deutsch. chem. Ges., **43,** 2684, 2692 (1910).
[7] Engler and Wöhler: Zeit. anorg. Chem., **29** (1909).
[8] Lefebure: Jour. Chem. Soc. **105,** 328 (1914).
[9] Reychler: Van Bemmelen Gedenkboek, 55 (1910).
[10] Freundlich: Kapillarchemie, 106 (1909).
[11] Zeit. anorg. Chem., **65,** 108 (1909).

grows smaller. Cushman and Coggeshall[1] found that a rock powder which would pass through a 200 mesh sieve surged like a liquid. When poured into a vessel, it only filled 46 percent of the space, while a coarser powder filled more. It is not surprising that the air-cushion around each particle makes the grains move one over another like a liquid. A similar phenomenon has been observed with ground phosphate rock. With a substance like carbon black, which adsorbs gases very markedly, as little as 5 percent of the apparent volume may be due to the carbon black[2] and a liter of carbon black may contain 2.5 liters of air.[3] When indigo is reduced to a very fine powder by means of a disintegrator[4] the single particles appear to be separated one from another by an envelope of air, so that the dry, solid powder occupies a space equal to that of a 20 percent paste of indigo, containing the same amount of indigo. Stoney[5] points out that the freedom of motion of finely divided solid particles becomes more marked when there is a temperature gradient. He cites the mobility imparted to very fine powders such as magnesium carbonate or precipitated silica by heating them in a metal dish. When the dish is disturbed the powder glides about as if floating whenever the powder is able by radiation to maintain a lower temperature than the dish.

Ives, Kingsbury and Karrer[6] state that the characteristics of thermocouples of varying diameter can be accounted for rather satisfactorily if it is assumed that they may be considered as cylindrical wires to which heat is conveyed through thin films of hot gas, of thickness independent of the temperature and size of the wire.

The presence of a film of air or vapor round a solid particle is shown in a striking way by the fact that it is quite a simple matter[7] to pass suspended phosphorus pentoxide through several wash-bottles in spite of its tremendously hygroscopic nature.

[1] Jour. Franklin Inst., **174,** 672 (1912).
[2] Cabot: Eighth Int. Congress Applied Chem. **12,** 18 (1912).
[3] Sabin: Technology of Paint and Varnish, 201 (1917).
[4] Jour. Soc. Dyers and Colourists, **17,** 294 (1901).
[5] Phil. Mag. (5) **4,** 443 (1877).
[6] Jour. Franklin Inst., **186,** 421 (1918).
[7] Engler and Wild: Ber. deutsch. chem. Ges., **29,** 1929 (1896).

Tyndall[1] found it very difficult to get experimental tubes which were absolutely clean on the surface and which contained no suspended particles. Dust-motes from the external air passed through U-tubes containing potash and sulphuric acid and through flasks containing ethers or alcohols. He states that it requires long-continued action on the part of an acid, first to wet the motes and then to destroy them.[2] The difficulty in stopping smokes in gas warfare is that the particles do not come in contact with the materials in the mask.

Schloesing[3] has put the thing generally by saying that it is much easier to take gas out of a gaseous mixture than to remove suspended liquid or solid particles. If the sheath of adsorbed air or gas is removed, wetting may take place. Since the sulphur trioxide from the contact process can be caught in concentrated acid and not satisfactorily in water, the concentrated acid must displace the gas film rapidly and fairly completely, while water does not; but we do not yet know the reason for this. One cannot agree with Knietsch[4] however when he says that it is a very remarkable and not satisfactorily explained fact that the sulphuric acid fog from the burner gases is more difficult to precipitate when it is cooled rapidly than when it is cooled slowly. Rapid cooling gives smaller particles and the air-cushion is larger relatively to the mass; consequently precipitation is more difficult.

Schuster[5] studied the disruptive discharge through gases and found an apparent diminution of dielectric strength with diminution of pressure. Since no sufficient decrease in inductive capacity could be observed in the mass of the gas, he assumed that layer in contact with the electrode there was a condensed surface of gas having a large inductive capacity. Schuster pointed out that some of the most puzzling facts of the disruptive discharge admit of explanation if we once admit the possibility of such a contact layer, diminishing in density with decreasing gas pressure. If this layer of adsorbed gas offers an increased resistance to the passage of an electrical discharge, it follows, from

[1] Phil. Trans., **160,** 337 (1870).
[2] See also Ehrenberg: Die Bodenkolloide, 226 (1915).
[3] Comptes rendus, **94,** 1187 (1882).
[4] Ber. deutsch., chem. Ges., **34,** 4081 (1901).
[5] Phil. Mag. (5) **29,** 197 (1880).

the Theorem of LeChatelier, that an electrical stress will tend to remove the film of adsorbed gas. This enables us to account for many apparently unrelated facts. Electrical waves will tend to remove active oxygen or active hydrogen from an electrode and will therefore cut down the over-voltage.[1] Superposing an alternating current on a direct current also decreases the over-voltage, making other reactions possible.[2] The experiments of Margules[3] and Ruer[4] on the dissolving of platinum find their explanation in the cutting down of the over-voltage.[5] With direct current there is oxidation to a higher and insoluble stage. With alternating current the over-voltage is decreased and little or none of the insoluble compound is formed. The electrolytic detector, the crystal detector, and the coherer, as used in wireless telegraphy, seem to owe their action to the partial or complete elimination of an air film by means of electrical stress. The essential difference between the coherer and the detector is that coalescence takes place readily in the former case and not in the latter.

It is interesting to note that Lenard[6] found that mercury wets platinum only when a current is flowing. At other times there is evidently an air film. It has been claimed by Allen[7] that the photo-electric fatigue of metals is due to a change in the surface film or gas or in the gas included in the metal (Hallwachs). It cannot be due to a chemical change such as oxidation; to a physical change such as roughening of the surface; to an electrical change in the formation of an electrical double layer (Lenard); or to a disintegration of the metal due to the expulsion of electrons by light (Ramsay and Spencer). The difference in the results

[1] Rothmund: Drude's Ann., **15,** 193 (1904); Bennewitz: Zeit. phys. Chem., **72,** 223 (1910).

[2] Archibald and von Wartenberg: Zeit. Elektrochemie, **17,** 812 (1911); Reitlinger: Ibid., **20,** 261 (1914); Ghosh: Jour. Am. Chem. Soc., **37,** 33 (1915); Stepanoff: Chem. Abstracts, **10,** 2431 (1916).

[3] Wied. Ann., **65,** 629; **66,** 540 (1898).

[4] Zeit. phys. Chem., **44,** 81, Zeit. Elektrochemie, **9,** 235 (1903); **11,** 10, 661 (1905); Haber: Zeit anorg. Chem., **51,** 365 (1906).

[5] Reitlinger: Zeit. Elektrochemie, **20,** 261 (1914).

[6] Wied. Ann., 30, 212 (1887).

[7] Phil. Mag. (6) **20,** 564 (1910); cf. Lenard: Drude's Ann., **8,** 196 (1902); **T2,** 490 (1903).

obtained by Allen may be due to the fact that Allen worked at atmospheric pressure, while Robinson's measurements were made on electrodes at a high vacuum.[1]

In cases of marked adsorption of gases it is interesting to determine what is the probable density of the adsorbed gas. Mitscherlich[2] calculated that, when carbon dioxide at atmospheric pressure and 12° is adsorbed by boxwood charcoal, the carbon dioxide occupies only one fifty-sixth of its original volume. Since this is a lesser volume than the same amount of carbon dioxide can occupy as a gas at this temperature, it is usually assumed that some of it has been liquefied. It is possible, however, to consider the carbon dioxide as present in the form of a highly condensed gas which has not liquefied. It might be interesting to study the behavior of carbon dioxide near the critical point in presence of charcoal. The magnitude of the heat of adsorption is an argument in favor of the actual liquefaction of the gas. Dewar[3] has calculated the apparent density of some gases adsorbed by cocoanut charcoal at low temperatures. The data in Table X show that the densities are of the same order as those of the liquid gases and are greater in some cases. At higher temperatures the amount of adsorption would be smaller and the apparent condensation less.

TABLE X.—DENSITY OF GASES ADSORBED BY CHARCOAL

Density in grams per cubic centimeter.

Gas adsorbed	Temperature of adsorption	Density of adsorbed gas	Density of liquefied gas
Carbon dioxide	+15	0.70	0.80
Oxygen	−183	1.33	1.12
Nitrogen	−193	1.00	0.84
Hydrogen	−193	0.06	0.07
Hydrogen	−210	0.08	
Hydrogen	−252	0.11	
Helium	−258	0.17	(0.122)

[1] Phil. Mag. (6) **23**, 255 (1912).

[2] Sitzungsber. Akad. Wiss. Berlin, **1841**, 376.

[3] Proc. Roy. Inst., **18**, 438 (1906).

It is to be noticed that the vapor pressure of a film of adsorbed gas in an apparently liquefied state stands in no relation to the vapor pressure of a mass of the liquefied gas. The phase rule generalization that the vapor pressure is constant for the system, liquid and vapor at constant temperature, holds good explicitly only in case the disturbing effects due to gravity, distortion of the solid masses, and capillary tensions are eliminated. So soon as a liquid film becomes thin enough so that the liquid no longer has the properties of matter in mass, the vapor pressure need not remain constant. When we have an adsorbed liquid or liquefied gas, the vapor pressure will vary also with the nature of the adsorbing agent. The lowering of the vapor pressure is shown by the fact that oatmeal,[1] previously dried at high temperature, has been used instead of sulphuric acid to produce the freezing of water under the receiver of an air-pump. L. J. Briggs[2] showed that the weight of the water film condensed on the surface of quartz at 30° in an atmosphere within one percent of saturation is 26.6 mg per square meter as determined by drying at 110°. This corresponds to a calculated thickness of the water film of 26.6$\mu\mu$ assuming the density of the film to be uniform and equal to unity. Neither assumption is absolutely accurate.

Since the amount of adsorption increases rapidly with falling temperature, adsorption must be accompanied by a marked evolution of heat. In Table XI the data not bracketted are by Favre.[3] All the molecular heats of adsorption are higher than the corresponding heats of liquefaction. The abnormally high values for hydrogen in palladium and platinum cannot be due to dissociation into monatomic hydrogen, because that would be accompanied by an adsorption of heat. They may be due in part to an oxidation of hydrogen. Masson[4] considers that the heat of adsorption of water vapor does not differ materially from the heat of liquefaction; but Dewar's data,[5] Table XII, confirm those of Favre, and we know also that there is always a

[1] Thomson: Phil. Mag. (4) **42,** 448 (1871).
[2] Jour. Phys. Chem., **9,** 617 (1905).
[3] Ann. Chim. Phys. (5) **1,** 209 (1874).
[4] Proc. Roy. Soc., **74,** 249 (1904).
[5] Dewar: Proc. Roy. Inst., **18,** 183 (1905).

heat effect when porous solids are wetted by liquids.[1] This is probably due to an actual increase in the density of the adsorbed liquid.

TABLE XI.—MOLECULAR HEATS OF ADSORPTION AND OF LIQUEFACTION OF GASES

Adsorbing agent	Gas	Adsorption g cal. per mol.	Liquefaction g cal. per mol.
Platinum	H_2	46,200	(240)
Palladium	H_2	18,000	(240)
Charcoal	NH_3	5,900— 8,500	(5,000)
Charcoal	CO_2	6,800— 7,800	6,250
Charcoal	N_2O	7,100— 7,700	4,400
Charcoal	SO_2	10,000—10,900	5,600
Charcoal	HCl	9,200—10,200	(3,600)
Charcoal	HBr	15,200—15,800	(4,000)
Charcoal	HI	21,000—23,000	(4,400)

Melsens[2] found that when 25 cc of different liquids were added to 10 grams of freshly ignited wood charcoal there was a rise of temperature of several degrees with ether, alcohol, and

TABLE XII.—MOLECULAR HEATS OF LIQUEFACTION AND ADSORPTION OF GASES

Charcoal as adsorbing agent at −185° (Dewar).

Gas	Adsorption g. cal. per mol.	Liquefaction, g. cal. per mol.
Hydrogen	1600	238
Nitrogen	3686	1372
Argon	3636	
Oxygen	3744	1664
Carbon monoxide	3416	

carbon bisulphide. When 97 grams of bromine were added to 11 grams of charcoal the rise of temperature was about 30°. Since a sudden compression of ten atmospheres raises the tem-

[1] Cf. POUILLET: Ann. Chim. Phys. (2) **20,** 141 (1822); CHAPPUIS: Wied. Ann. **19,** 21 (1883); MARTINE: Phil. Mag. (5) **47,** 329 (1889); **50,** 618 (1900); (6) **15,** 595 (1903); PARKS: Ibid. (6) **4,** 240 (1902); **5,** 517 (1903).

[2] Ann. Chim. Phys. (5) **3,** 522 (1874).

perature of water only 1/77 of a degree he concluded that the rise of temperature of 1.16° when charcoal is wetted by water corresponds to a pressure of 893 atmospheres. Calculating in the same way he drew the conclusion that the force of adsorption is 3100 atmospheres for bromine, 13,090 for carbon bisulphide, 4620 for ether and 3080 for alcohol.

Gaudechon[1] obtained the data given in Table XIII for different liquids, with wood charcoal. Since the heat of liquefaction varies with the temperature, it is probable that the heat of adsorption of gases and vapors does also; but this point seems not to have received any special attention.

TABLE XIII.—HEAT EVOLUTION ON WETTING WOOD CHARCOAL

Gram calories per gram charcoal.

	g. cal.		g. cal.
Water	3.9	Acetone	3.6
Methyl alcohol	11.5	Chloroform	2.3
Ethyl alcohol	6.9	Ether	1.2
Propyl alcohol	5.6	Benzene	4.2
Amyl alcohol	3.7	CCl_4	1.5
Formic acid	12.0	CS_2	4.0
Acetic acid	6.0	C_5H_{12}	0.4

Lamb and Coolidge[2] find that curves, which approximate closely to straight lines, are obtained when the heats of adsorption of the vapors of some organic liquids by charcoal are plotted against the amounts adsorbed. The difference between the heat of adsorption and the heat of vaporization is called by them the net heat of adsorption and is practically constant for the different liquids studied, when referred to equal volumes of adsorbed liquid. Assuming that this net heat of adsorption is a heat of compression, the attracting force is estimated to be about 37,000 atmospheres when one cubic centimeter of liquid is adsorbed by ten grams of charcoal.

The action of water vapor on cotton has been studied by

[1] Comptes rendus, **157,** 209 (1913).

[2] Jour. Am. Chem. Soc. **42,** 1146 (1920).

Beadle[1] and by Masson.[2] If the bulb of a thermometer be covered with carefully dried cotton wool, and if the bulb be then dipped in a beaker or water at the same temperature, the thermometer will rise 8°–12° or even more. The relatively large amount of air which is always entangled in the cotton wool does not escape during or after immersion, and the fibers present a glistening appearance under water, which suggest that they are not wetted completely. Medicated or absorbent cotton differs from the ordinary, nearly pure, material in that the former has been freed from traces of natural cotton wax by treatment with solvents. When absorbent cotton is dipped into water, the rise in temperature is less than in the previous case even though more water is taken up by the cotton. In the case of the nearly pure cotton wool, the water evidently distills across the air space, while there is a certain amount of direct wetting with the absorbent cotton. There should therefore be a marked evolution of heat if cotton is placed in saturated water vapor and the two cottons should behave exactly alike. Both these predictions were confirmed experimentally. Masson obtained similar results when guncotton or glass wool was exposed to saturated water vapor or cotton to the vapor of absolute alcohol; but the heat effects were much smaller in these instances owing to the lesser adsorption.

L. B. Loeb[3] finds that the adsorption of methyl alcohol vapor by 0.41g platinum black causes a rise of temperature of about 0.36° when there is no oxidation.

The effect of traces of impurity on the adsorption is shown in some experiments by Berliner.[4] His purified palladium foil adsorbed about 860 volumes of hydrogen. If allowed to stand in a vacuum for an hour, it then adsorbed practically no hydrogen. If left for an hour or two in the air, the same thing happened. The disturbing factor is apparently a trace of grease, because water did not wet the soiled palladium. Similar results were obtained with platinum.

[1] Nature, **49**, 457 (1884); Chem. News, **71**, 1 (1895); **73**, 180 (1896).

[2] Proc. Roy. Soc., **74**, 230 (1904); Masson and Richards: Ibid., **78A**, 412 (1906).

[3] Proc. Nat. Acad. Sci., **6**, 107 (1920).

[4] Wied. Ann., **35**, 803 (1888).

The Adsorption Isotherm

So far we have only committed ourselves to the qualitative statement that the amount of adsorption increases with increase of pressure. It is now advisable to consider the quantitative side. Dewar[1] has made some measurements with hydrogen at varying pressures in charcoal at −185°. The results are given in Table XIV. Dewar says in regard to them that the amount adsorbed is seen to increase with the pressure to 10 atmospheres, after which the adsorption in the pores of the charcoal seems to be independent of the pressure. At the temperature of liquid air this sample of charcoal (6.7 g) would not adsorb more than about one liter of hydrogen even when the pressure was raised from 10 to 25 atmospheres. It appears that Dewar considers the decrease from 156 cc to 138 cc as due to experimental error for he says distinctly that the adsorption had come to a limit. Since that time a number of careful investigations have been made on the quantitative variation of the adsorption with the pressure.[2]

Table XIV.—Hydrogen Adsorbed by Charcoal at −185°

Atm.	cc/gram	Atm.	cc/gram
1	92	15	149
5	138	20	145
10	156	25	138

If we plot the amounts of adsorbed gas against the pressures, we get the so-called adsorption isotherm, a smooth curve concave to the pressure axis. Trouton[3] obtained a curve with the opposite flexure for the adsorption of water by flannel; but Masson[4]

[1] Proc. Roy. Inst., **18,** 437 (1906).

[2] Travers: Proc. Roy. Soc., **78A,** 9 (1906); Davis: Jour. Chem. Soc., **91,** 1066 (1907); Geddes: Drude's Ann., **29,** 797, (1907); Boyle: Jour. Phys. Chem., **12,** 484 (1908); Phil. Mag. (6) **17,** 377 (1909); McBain: Ibid **18,** 916 (1909); Zeit. phys. Chem., **68,** 471 (1909); Homfray: Ibid., **74,** 139, 687 (1910); Titoff: Ibid., **74,** 641 (1910); Piutti and Maglia: Gazz. chim. ital., **40** I, 569 (1910).

[3] Proc. Roy. Soc., **77A,** 292 (1905).

[4] Ibid., **78A,** 9 (1906).

obtained normal curves for water and cotton, and Travers[1] obtained normal curves for wool and cotton with water vapor, so that Trouton's results are apparently due to experimental

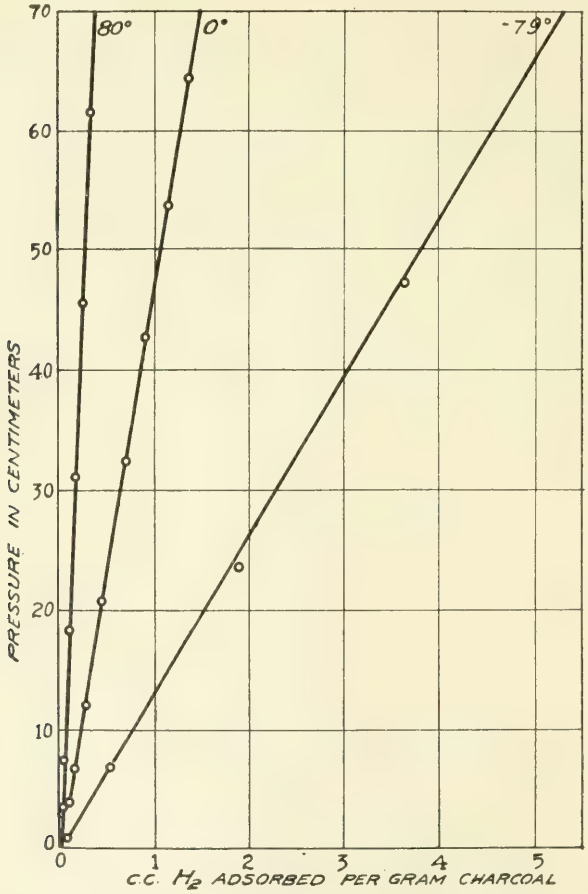


FIG. 1.

error. Trouton[2] also obtained an abnormal type of curve for the adsorption of water vapor by glass; but it seems probable that alkali dissolved from the glass has been a disturbing factor.

[1] Proc. Roy. Soc., **79A**, 204 (1906).
[2] Ibid., **79A**, 383 (1906).

If the gas is adsorbed but slightly, the curve may seem practically a straight line over the ordinary pressure ranges. This is shown very clearly in the curves for hydrogen in charcoal Fig. 1 as determined by Titoff.[1] If the gas is adsorbed strongly, the isotherm bends around so as to run nearly parallel with the pressure axis, because then a marked increase in pressure causes

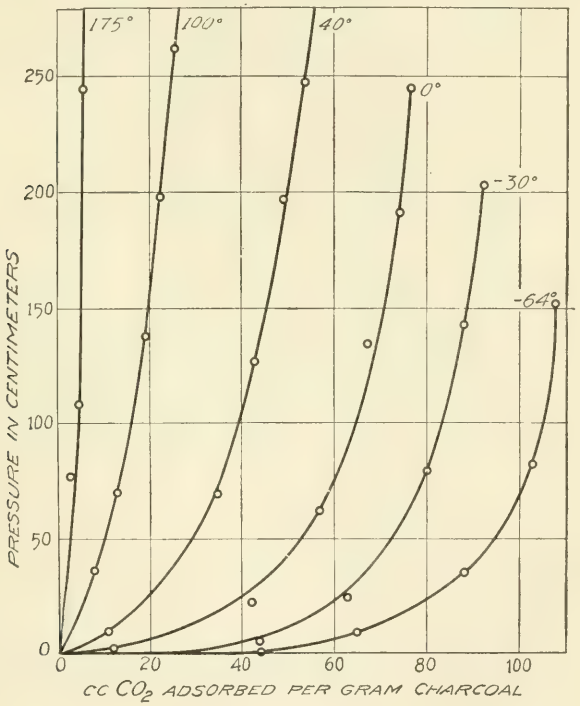


FIG. 2.

only a relatively slight increase in adsorption. These two extremes can be realized very well with ammonia and charcoal[2] at 175° and −64°, Fig. 2. In Table XV are given Titoff's data for the adsorption of ammonia by charcoal at 0° and at 151.5°. Under $\Delta x/\Delta y$ is given the mean increase in adsorption with increase of pressure between each two consecutive observations.

[1] Zeit. phys. Chem., **74,** 641 (1910).

[2] RICHARDSON: Jour. Am. Chem. Soc., **38,** 1828 (1917).

At 0° the values drop from 92 to 3, a ratio of over 30:1, while at 151.5°, the drop is only from 51 to 11, a ratio of less than 5:1.

If we plot the logarithms of the amounts of adsorbed gas

TABLE XV.—ADSORPTION OF AMMONIA BY CHARCOAL

Temperature 0°			Temperature 151.5°		
Pressure in mm	Adsorption in cc	Δx/Δy cc/mm	Pressure in mm	Adsorption in cc	Δx/Δy cc/mm
2.9	5.4		2.8	0.3	
28.8	30.2	0.92	16.6	1.0	0.051
78.7	60.4	0.65	64.8	2.1	0.021
161.0	90.3	0.36	176.2	4.0	0.018
319.2	115.7	0.16	285.0	5.5	0.013
490.0	127.0	0.07	432.7	7.2	0.012
636.4	132.4	0.04	576.8	8.9	0.012
746.7	135.9	0.03	721.8	10.5	0.011

against the logarithms of the pressures, we get a curve which approximates a straight line, especially if the gas is not adsorbed too much. This shows that the data can be represented approximately by an equation[1] of the form $(x/m)^n = kp$, where x is the

TABLE XVI.—ADSORPTION OF CARBON DIOXIDE BY CHARCOAL

Formula $x^{1.77}/p = 0.0602$.
x = cc CO_2 adsorbed per cc charcoal.
p = pressure in mm Hg. Temp. 31°.

p	x found	x calc.	p	x found	x calc.
41.5	1.7	1.7	453	6.5	6.4
120.	2.9	3.1	534	7.1	7.1
194.	4.0	4.0	602	7.6	7.6
276.	4.7	4.9	678	8.3	8.2
340.	5.4	5.5	698	8.6	8.3
405.	5.9	6.0	703	8.9	8.4

amount of gas adsorbed and m the amount of the adsorbing solid, while p is the pressure and k and n are constants to be determined experimentally for each temperature. The expo-

[1] Chemists are in the habit of calling this an exponential formula which is not correct in the strict mathematical sense; but which is justified by usage.

nential factor, n, is usually not an integer and its physical significance is unknown.[1] In Table XVI are given some data by Geddes[2] on the adsorption of CO_2 by charcoal. The formula enables us to calculate the adsorption with a moderate degree of accuracy. Of course data could have been picked out which would have looked better, but there seems no advantage in doing this. The formula cannot possibly represent the facts for pressures at which the curve runs nearly parallel to the pressure axis, and the experiments of Richardson[3] on the adsorption

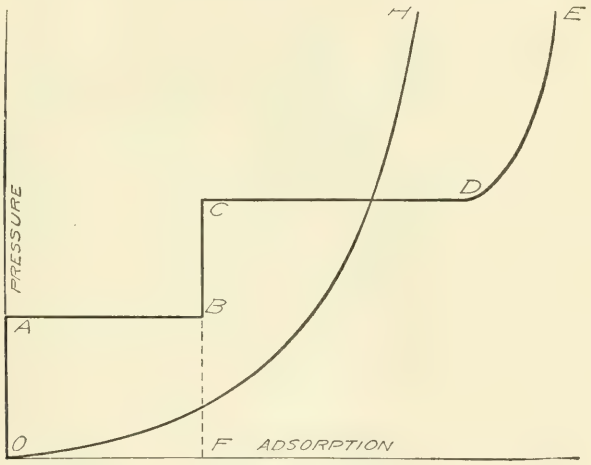


FIG. 3.

of ammonia by charcoal makes it probable that the equation never describes the facts accurately over any wide range of pressures. For the present it should be considered as a serviceable interpolation formula, though it may possibly belong in the same category as the simple gas law.

The fact that we get a smooth curve when plotting pressure direct against adsorption shows that no definite compound is formed. In Fig. 3 the pressure is plotted along the vertical axis and the amount of gas condensed on or by unit mass is

[1] For a slightly different formulation, see WILLIAMS: Trans. Faraday Soc., **10,** 167 (1914); Proc. Roy. Soc., Edinburgh, **391,** 48 (1919).

[2] Drude's Ann., **29,** 797 (1909).

[3] Jour. Am. Chem. Soc., **38,** 1828 (1917).

plotted along the horizontal axis. The typical adsorption isotherm is represented by the curve OH, while OABCDE is the curve (not to scale) for the taking up of water by sodium sulphate. Along OA the solid phase is anhydrous sodium sulphate. Along AB the pressure remains constant because three phases are present: Na_2SO_4, $Na_2SO_4.10H_2O$, and water vapor. Along BC the pressures change without any more water being taken up and consequently there are only two phases, water vapor and the compound $Na_2SO_4.10H_2O$. The composition of the compound is given by F, the point at which the prolongation of CB cuts the axis of abscissas. Along CD the phases are $Na_2SO_4.10H_2O$, saturated solution and vapor, so the pressure remains constant, while unsaturated solution and vapor coexist along the curve DE. Many curves of this type have been determined by Browne[1] and others in his laboratory for the ammonia compounds. The curve OH is clearly not of this type and represents either a continuous series of solid solutions or an adsorption. The equilibrium is usually reached fairly rapidly, which is an argument against the existence of a solid solution though by no means a conclusive one. More convincing is the fact that the amount of adsorption by charcoal varies with the structure[2] and the extent of surface. The change produced by grinding charcoal[3] is only a slight one, because the surface of the unground charcoal is so enormous. Lagergren[4] estimates that one gram of charcoal has a surface of four square meters and is composed of about 1.4 billion particles. Lamb, Wilson and Chaney[5] consider that one cubic centimeter of active war charcoal has a surface of about 1000 square meters (density about 0.4).

While the experiments on the taking up of gases by charcoal show fairly conclusively that surface phenomena are the important ones, there is always the possibility that a solid solution may also be formed to some extent. McBain[6] considers that

[1] See Browne and Houlehan: Jour. Am. Chem. Soc., **35,** 649 (1913).

[2] Piutti and Maglia: Gazz. chim. ital., **40 I,** 569 (1910).

[3] Chappuis: Wied. Ann., **12,** 164 (1881). Cf. also Gurwitsch: Zeit. Kolloidchemie, **11,** 17 (1912).

[4] See Van Bemmelen: Die Absorption, 410 (1910).

[5] Jour. Ind. Eng. Chem., **11,** 420 (1919).

[6] Phil. Mag. (6) **18,** 916; Zeit. phys. Chem., **68,** 471 (1909).

over 13 percent of the hydrogen taken up by cocoanut charcoal at the temperature of liquid air is present as a solid solution.[1] On the other hand Titoff[2] believes that the amount of hydrogen dissolved in the charcoal has been over-estimated by McBain.[3] The truth of the matter is that we have no definite criterion which will enable us to distinguish accurately in all cases between solid solution and adsorption. In the case of cellulose and of gelatine it is quite possible that some water is actually dissolved. Until we know more about the subject it is safer to treat any doubtful case as chiefly one of adsorption.

On the other hand, the two special cases of metals and rubber with gases call for some special comment. Assuming the existence of pores in platinum or palladium foil, one can account for the selective diffusion of hydrogen by postulating adsorption in the pores and subsequent diffusion. At high temperatures the adsorption would be much less, and it is difficult to explain the increased rate of selective diffusion. It is simpler to account for the diffusion of hydrogen through platinum by postulating that some of the hydrogen actually dissolves in the platinum. In that case the solubility should be independent of the physical structure of the platinum. This seems to be true within narrow limits for platinum and within wide limits for palladium. It seems probable that platinum can dissolve several volumes of hydrogen at ordinary temperatures, and palladium nearly eight hundred volumes.[4] The bulk of the hundred volumes of hydrogen which are taken up by platinum black[5] must be adsorbed, and the same must be true of the nearly 3000 volumes taken up by colloidal platinum.[6] This is apparently the conclusion reached by Holt, Edgar, and Firth.[7] If platinum and palladium dissolve hydro-

[1] Cf. Travers: Proc. Roy. Soc., **78A,** 9 (1906).

[2] Zeit. phys. Chem., **74,** 641 (1910).

[3] For other discussions, see Masson: Proc. Roy. Soc., **74,** 251 (1904); Davis: Jour. Chem. Soc., **91,** 1066 (1907); Geddes: Drude's Ann., **29,** 797 (1908); Wöhler, Pluddemann and Wöhler: Zeit. phys. Chem., **62,** 670 (1908); Homfray: Ibid., **74,** 139, 687 (1910).

[4] Cf. Bose: Zeit. phys. Chem., **34,** 708 (1900).

[5] Ramsay, Mond and Shields: Zeit. phys. Chem., **19,** 40 (1896); **25,** 657 (1898).

[6] Paal and Gerum: Ber. deutsch. chem. Ges., **41,** 805 (1908).

[7] Zeit. phys. Chem., **82,** 513 (1913).

gen to some extent, the passage of carbon monoxide through heated iron cannot be attributed to adsorption. At present it is not possible to say whether an iron carbonyl plays any part in the diffusion or not. In the case of platinum and oxygen Ramsay, Mond, and Shields[1] consider that most of the oxygen taken up forms $Pt(OH)_2$. They point out that Thomsen obtained an evolution of heat of 17,000 calories for the reaction $Pt+O+H_2O$, while they find 17,600 calories for the so-called adsorption of sixteen grams of oxygen by platinum.

In view of the relative behavior of rubber with water and with pyridine, it is hard to see how the permeability can be a question primarily of adsorption. I think that we must assume that carbon dioxide, pyridine, etc., actually dissolve in rubber.

TABLE XVII.—ADSORPTION OF CARBON DIOXIDE BY BLOOD CHARCOAL

Formula $x/p = 0.00024$.
x = millimols CO_2 per gram charcoal.
p = partial pressure in mm Hg.
Temperature 20°.

p	x	k	p	x	k
613.1	0.1461	0.00024	337.7	0.0855	0.00025
611.1	0.1424	0.00023	325.5	0.0808	0.00025
605.	0.1320	0.00022	312.2	0.0706	0.00023
453.1	0.1014	0.00022	229.	0.0560	0.00024
437.2	0.1086	0.00025	221.2	0.0523	0.00023
435.2	0.1063	0.00024	176.	0.0452	0.00026
348.5	0.0844	0.00024	170.2	0.0451	0.00026
339.	0.088	0.00026		mean	0.00024

While the equation $x/m = kp$ is a special case of the equation $(x/m)^n = kp$, where $n = 1$, and therefore may hold even in cases of adsorption, it is also the simplest case of Henry's law for the solubility of gases in liquids. Reychler[2] found that the amount of carbon dioxide taken up by blood charcoal was proportional to the partial pressure of the carbon dioxide in the vapor phase. The data are given in Table XVII. It does not

[1] Ibid., **25,** 684 (1898).
[2] Van Bemmelen Gedenkboek, 55 (1910).

seem probable that CO_2 dissolves in carbon, and I prefer to consider this a case of adsorption where the exponential factor happens to be unity. This view is confirmed by the fact that Geddes obtained very different relations for the adsorption of CO_2 by charcoal at 31° (Table XVI).

Reychler also found that the amount of carbon dioxide taken up by rubber was proportional to the pressure over a narrow range of pressures. This may well be a case of solution of carbon dioxide in rubber.

The concentration-pressure curve for hydrogen and palladium[1] has two ascending branches connected by a branch which is nearly but not quite, parallel to the concentration axis. It is not known to what extent the peculiarities of this curve are due to adsorption.

While many people are willing to speak of adsorption and to let it go at that, attempts have been made to account for adsorption either through the formation of known or unknown compounds. Rhead and Wheeler[2] consider that the fixation of oxygen by carbon involves the formation of a compound, C_xO_y, which breaks up into carbon dioxide and carbon monoxide when heated. Haber[3] points out that, according to Bragg, the ordinary solid crystalline salts are not systems in which one anion and one cation form a molecule which is separated from the next; but that one anion is probably bound to all the surrounding cations. Unless the outer layer of a crystal differs fundamentally from the inner portions, there must be forces at the surface of the crystal similar to those acting between the outer layer and the next layer. If we call these forces chemical valences of some sort, it is possible that adsorption is due essentially to the saturation of these valences. These ideas have been developed by Langmuir[4] as a result of his experiments on electrically heated carbon and other filaments in presence of oxygen at pressures of 0.004–0.007 mm. Langmuir considers that any crystal or

[1] Hoitsema: Zeit. phys. Chem., **17,** 1 (1895); Ramsay, Mond, and Shields: Ibid., **19,** 25 (1896); Holt, Edgar and Firth: Jour. Chem. Soc., **82,** 513 (1913).

[2] Jour. Chem. Soc., **103,** 462 (1913).

[3] Jour. Soc. Chem. Ind., **33,** 50; Zeit. Elektrochemie, **20,** 521 (1914).

[4] Jour. Am. Chem. Soc., **37,** 1139 (1915); **38,** 1145, 2221 (1916).

any mass of liquid forms a giant molecule, and that an adsorbed gas forms a compound with the outer layer, the thickness of the reacting gas film being rarely over one or two molecules thick. Looking at the subject from a kinetic point of view he deduces an equation of the form

$$Q = \frac{1}{\frac{a}{p} + b - cp}$$

where Q is the amount adsorbed at the pressure p, and a, b and c are constants.

There are two independent questions involved in Langmuir's hypothesis, namely whether the maximum adsorption film is only one or two molecules thick and whether this layer forms a compound with the adsorbing agent. The first may be true and the second be wrong. Langmuir claims that the adsorbed film never exceeds two molecules in thickness for plane surfaces, though he is apparently willing to concede a greater thickness for porous substances. There is no question but that the adsorption film is very thin. Mitscherlich[1] calculates a thickness of about $50\mu\mu$ for carbon dioxide adsorbed by charcoal, and the film of water round each particle of clay[2] is usually assumed to be of the same thickness, while L. J. Briggs[3] estimates about $27\mu\mu$ for the film of water on quartz. It is difficult to be certain on these points because one does not know the surface with any degree of accuracy; but the evidence is in favor of Langmuir's contention.

When it comes to the question of whether compounds are formed or not, it must be remembered that Langmuir uses the word molecule in a new sense. He considers that the oceans and all that in them is constitute one vast molecule and that catching a fish is a chemical reaction because it breaks up the molecule. This may be perfectly true; but the usefulness of it has not been made clear. For the present, it seems much wiser to say that one substance adsorbs another selectively, meaning that the concentration at the surface of the phase has increased. Whenever there is no proof that a compound is formed of the type at

[1] Sitzungsber. Akad. Wiss. Berlin, **1841**, 379.

[2] Cf. Davis: Trans. Am. Ceramic Soc., **15**, 69 (1913).

[3] Jour. Phys. Chem., **9**, 617 (1905).

present recognized by chemists, it is safer not to postulate the existence of compounds. When the time comes that it is a distinct advantage to distinguish an entirely new type of compound, an indefinite chemical compound, that can be done; but hopeless confusion will arise whenever a man uses a word in one sense and his listeners in another. It is quite probable that a more careful study of contact catalysis may force us to adopt Langmuir's view or some modification of it; but it will then be necessary to gather in a lot of the loose ends.

In some cases compounds are undoubtedly formed. Thus when platinum black takes up oxygen, a portion of the oxygen is certainly present as oxide. On the other hand, it seems improbable that it would be so difficult to make carbon tetrachloride direct if the chlorine, which is adsorbed by charcoal and thereby made active,[1] consisted of a normal compound of carbon and chlorine. While the oxidizing action of platinum may be due to a platinum oxide, this cannot be true in the case of charcoal and oxygen. Calvert[2] showed that oxygen adsorbed by charcoal will oxidize ethyl alcohol to acetic acid and ethylene to carbon dioxide and water, reactions which certainly cannot be due to any known oxide of carbon. It also seems unsatisfactory to postulate that the noble gases form definite chemical compounds with charcoal.

Years ago Angus Smith[3] ignored the variation of adsorption with the pressure and concluded that at atmospheric pressure charcoal adsorbed gases in volumes which were multiples of the volumes of hydrogen adsorbed. His figures were: hydrogen, 1; oxygen, 7.99; carbon monoxide, 6.03; carbon dioxide, 22.05; methane, 10.01; nitrous oxide, 12.90; sulphur dioxide, 36.95; nitrogen, 4.66. Smith lays stress on the fact that the 22 for carbon dioxide and the 10 for methane can be considered as $6 + 16$ and $6 + 4$ respectively, though it is difficult to see what this proves. In order to make the value for nitrogen seem plausible, Smith points out that $14 \times 4.66 = (14)^{\frac{2}{3}}$; but these calculations are only of historical interest now.

[1] Damoiseau: Comptes rendus, **73,** 60 (1876).
[2] Jour. Chem. Soc., **20,** 293 (1867).
[3] Chem. News, **18,** 21 (1868); Proc. Roy. Soc., **28,** 322 (1879).

Chemical Reactions

Since reaction velocity is probably directly proportional to the difference of chemical potential and inversely proportional to the chemical resistance, we can increase the reaction velocity either by increasing the difference of chemical potential or by decreasing the chemical resistance. The increased concentration due to adsorption at the surface of a solid will necessarily cause an increase in reaction velocity quite apart from any catalytic action which the solid may exert.[1] In the form of wood ashes, charcoal is often used in outhouses and elsewhere to eliminate unpleasant odors. The charcoal adsorbs the odoriferous substances and then accelerates their oxidation by oxygen which is adsorbed from the air. Shenstone[2] invented a respirator filled with powdered wood charcoal to be worn in hospitals and which should adsorb and then destroy germs of cholera and other diseases. This was the forerunner of the modern gas mask. It is not known whether the oxidizing action of the charcoal is due to anything more than the increase in concentration of the oxygen.

As a matter of fact, the effect of concentration seems to be relatively unimportant in most of the cases studied hitherto. Patrick's silica gel has a surface of 2.5×10^8 cm^2 per gram and is an excellent adsorbent, but, so far, it does not have any marked catalytic effect except in the oxidation of nitric oxide. It would be interesting to try this substance at 100° with the mixed vapors of alcohol and acetic acid, because this reaction takes place at a measurable rate in the vapor phase in the absence of any catalytic agent. It is stated that oxyhydrogen gas has been found to be quite stable under pressures of two thousand atmospheres, which shows that the catalytic action of platinum on mixtures of hydrogen and oxygen must be due to something more than a change in concentration. The marked difference in the behavior of platinum and charcoal toward oxyhydrogen gas is another argument in favor of the action of a catalytic agent being specific. On the other hand Hempel[3] with SO_2 and O_2 obtained a yield

[1] See, however, Langmuir: Jour. Am. Chem. Soc., **38,** 2286 (1916).

[2] Pharm. Jour., **13,** 454 (1854).

[3] Ber. deutsch. chem. Ges., **23,** 445 (1890).

of 65 percent SO_3 without any catalytic agent by working at a pressure of thirty to forty atmospheres.

If we have selective adsorption of the reaction products, this will cause a lowering of the chemical potential of the resultants[1] and will therefore increase the reaction velocity. It may even determine the direction of the reaction. Alcohol breaks down into acetaldehyde and hydrogen in presence of pulverulent nickel and into ethylene and water in presence of pulverulent alumina or silica.[2] Since nickel adsorbs hydrogen strongly and alumina adsorbs water,[3] it seems natural to assume that the selective adsorption is the determining factor.[4]

While this seems very satisfactory, there are certain points which must not be overlooked. When making ethylene at Edgewood Arsenal during the war, it was found advisable to have a large amount of steam present with the alcohol vapor in order to make temperature regulation easier. This undoubtedly decreased the rate of decomposition of the alcohol; but that difficulty was overcome by working at a higher temperature. It is very difficult to see how alumina can dehydrate alcohol in presence of a large amount of water vapor if the reason the alumina acts is because of its strong adsorption of water vapor. Since there seems very little probability of accounting for the various decompositions of the esters on the basis of selective adsorption of the reaction products, it is probable that a complete explanation of the phenomena of contact catalysis is not to be found along these lines.

If changes in the chemical potential are not the important factors in contact catalysis, the catalytic agent must change the chemical resistance in some way, and there are two possible ways in which this might happen. We may have more effective collisions between existing molecules or we may have a conversion of one or more of the reacting substances into an active form.

According to the kinetic theory the reaction velocity is pro-

[1] W. C. McC. Lewis suggests the terms reactants and resultants for reacting substances and reaction products.

[2] Ipatieff: Ber. deutsch. chem. Ges., **34,** 3579 (1901); **35,** 1047, 1057, (1902) **36,** 1990, 2003, 2014, 2016 (1903); Sabatier and Senderens: Comptes rendus, **136,** 738, 921, 936, 983 (1903).

[3] Johnson: Jour. Am. Chem. Soc., **34,** 911 (1912).

[4] Engelder: Jour. Phys. Chem., **21,** 676 (1917).

portional to the number of collisions between possibly reacting molecules; but it does not follow at all that two molecules react every time they collide. If a large number of collisions is necessary on an average before a pair of molecules react, anything which would make these collisions more helpful might increase the reaction velocity enormously. The first question is then whether there is any evidence of ineffective collisions. This matter has been studied by Strutt[1] who comes to the conclusion that a molecule of ozone reacts every time it strikes a molecule of silver oxide; but that a molecule of active nitrogen collides with a molecule of copper oxide five hundred times on an average before they react, while two molecules of ozone at 100° collide on an average 6×10^{11} times before they react. Without insisting on the absolute accuracy of these figures there is evidently plenty of margin for an increase in reaction velocity with ozone at 100° if one could produce more effective collisions. Langmuir[2] finds that 15 percent of all oxygen molecules at a pressure of not over 5 bars striking a tungsten filament at 1770°K react with it to form tungstic oxide, WO_3. This coefficient increases at higher temperatures and at 3300°K about 50 percent of all the oxygen molecules which strike the filament react with it to form WO_3. Since there are three atoms of oxygen in WO_3 and only two in the oxygen molecule, Langmuir considers that at least one-half of the tungsten surface must be covered at 3300°K with oxygen in some form.

It is possible that a catalytic agent may cause one molecule to strike another amidships instead of head-on and may thereby increase the effectiveness of the collisions. It is not impossible that part at least of the effect of solvents on reaction velocity may be due to some such thing as this. If we adopt Langmuir's views[3] of oriented adsorption, all sorts of things become possible. If ethyl acetate, for instance, attaches itself to one adsorbent by the methyl group, to another by the ethyl group, and to a third by the carboxyl group, it might very well be that bombardment of the captive molecule by free ones might lead to very different reaction products in the three cases. Such a suggestion

[1] Proc. Roy. Soc., **87A,** 302 (1912).
[2] Jour. Am. Chem. Soc., **35,** 105 (1913); **38,** 2270 (1916).
[3] Cf. Debus: Jour. Chem. Soc., **53,** 327 (1888).

is of very little value, however, unless it can be made definite. We do not know as yet whether ethyl acetate is actually adsorbed in one way by nickel, in another way by thoria, and in a third way by titania, nor do we know whether the difference in the manner of adsorption, assuming it to occur, is of such a nature as to account for the differences in the reaction products. It may well be that some entirely different hypothesis will prove necessary. The general problem of increasing the effectiveness of molecular collisions is distinctly an important one which has not been studied at all.

There is one special case in which we can apparently identify one of the factors of chemical resistance. Buchböck[1] studied the decomposition of carbonyl sulphide and found that the reaction velocity decreased with increasing viscosity of the solution. Since the reaction products are gases, this suggests the possibility that the retardation is due to the greater difficulty of forming gas bubbles in a more viscous medium. This receives confirmation from Raschig's work on the preparation of hydrazine,[2] by the action of hypochlorite on ammonia, the evolution of nitrogen being kept down by something like starch to make the solution more viscous. The preliminary reaction is $NH_3 + NaClO = NH_2Cl + NaOH$ and high viscosity promotes the reaction $NH_2Cl + NH_3 = N_2H_4HCl$ as against the one $3NH_2Cl + 2NH_3 = 3NH_4Cl + N_2$.

Instead of more effective collisions between unchanged portions of the reacting molecules we may have a partial conversion of one or more of the reacting substances into active forms either through the rupture of normal valences or of contra-valences, opening up fields of force as Baly[3] puts it.

The conception of Baly that a catalytic agent activates the reacting substances by opening up fields of force covers the ground admirably as a purely formal statement. The trouble with it is that it is as yet too vague to be of any value as a working hypothesis, though it is undoubtedly the best starting-point. It is necessary to show in each particular case just what happens and why it happens. While the conversion of a reacting sub-

[1] Zeit. phys. Chem., **23,** 123 (1897); **34,** 229 (1900).

[2] Henderson: Catalysis in Industrial Chemistry, 60 (1919).

[3] Jour. Chem. Soc., **101,** 1469, 1475 (1912).

stance into an active form may very well account for the effect of the solvent on reaction velocity in homogeneous systems, it must be shown what active form is produced and why one solvent produces more of it than another. Activation may lead to the formation of intermediate compounds or it may not; but we have got to get down to more definiteness in all the cases of contact catalysis. It is often assumed that definite intermediate compounds are formed and this is certainly true in some cases. In the catalysis of hydrogen peroxide by mercury, the intermediate formation of mercuric peroxide can be detected by the eye because there is an intermittent formation of a film, which then breaks down, only to form again.[1] The formation of graphite is usually preceded by the formation of a carbide. The conversion of acetic acid into acetone[2] by passing the vapor over heated barium carbonate presumably involves the intermediate formation of barium acetate, though one cannot ear-mark the carbon dioxide and so cannot be absolutely certain that the barium carbonate is continually decomposed and regenerated. In the Deacon chlorine process, where a mixture of hydrochloric acid and oxygen is passed over heated cupric chloride, Hurter[3] assumes the existence of an intermediate compound. People are not agreed, however, whether the intermediate compound is cuprous chloride, cupric oxychloride, or both. The extreme sensitiveness of this reaction to poisons raises a question whether an intermediate compound really is formed. In the catalytic oxidation of carbon monoxide, it is usually believed that there is alternate reduction and oxidation of the oxides which act as catalytic agents.

Sabatier[4] believes that the catalytic action of alumina on alcohol is due to the intermediate formation of an instable compound of alumina and water. On the other hand, Henderson[5] assumes the intermediate formation of aluminum ethylate. Neither one offers any experimental evidence in support of his

[1] Bredig and von Antropoff: Zeit. Elektrochemie, **12,** 581 (1906); von Antropoff: Jour. prakt. Chem. (2) **77,** 273 (1908).

[2] Squibb: Jour. Am. Chem. Soc., **17,** 187 (1895).

[3] Jour. Soc. Chem. Ind., **2,** 106 (1883).

[4] Die Katalyse in der organischen Chemie, 240 (1914).

[5] Catalysis in Industrial Chemistry, 4 (1919).

belief, and neither one discusses why kaolin should act practically as well as alumina.

It seems probable that the best way to solve the problem of contact catalysis is to start with the side which has been neglected a good deal and to study the selective action of catalytic agents. Quite apart from any theory we may adopt, there are certain questions which ought to be answered experimentally and yet these questions have not even been raised in a serious way. We know that ethyl alcohol can be decomposed into acetaldehyde and hydrogen or into ethylene and water but that is practically all that we know as yet about these reactions. With pulverulent nickel the reaction is almost completely

$$CH_3CH_2OH = CH_3CH_2O + H_2$$

We do not know whether the hydrogen comes off in one stage or in two. If it comes off in two stages, is the first stage CH_3CH_2O or CH_3CHOH? While it may not be easy to devise a method which will answer this question, the problem is not more difficult than many which the organic chemists have solved successfully.

With pulverulent alumina the reaction is almost completely

$$CH_3CH_2OH = CH_2CH_2 + H_2O.$$

Does water split off as such or do we get the splitting off of hydroxyl or hydrogen? It seems improbable that water can split off as such because then it would be difficult to account for the intermediate formation of ether. If the first stage is a splitting off of hydroxyl does the other hydrogen come from the adjacent carbon atom giving ethylene direct or does it come from the same carbon atom, forming a substituted methylene, CH_3CH, which then rearranges to ethylene? One would also like to know what nickel does with diethyl ether.

With nickel we get the following decomposition of the esters:

$$CH_3CO_2CH_2CH_3 = CH_3CH_2CH_3 + CO_2$$
$$CH_3CO_2CH_3 = CH_3CH_3 + CO_2$$
$$HCO_2CH_3(?) = CH_4 + CO_2$$

With thoria the decomposition is quite different:

$$2CH_3CO_2C_2H_2 = CH_3COCH_3 + CO_2 + (C_2H_5)_2O$$
$$= CH_3COCH_3 + CO_2 + C_2H_5OH + C_2H_4$$
$$2CH_3CO_2CH_3 = CH_3COCH_3 + CO_2 + (CH_3)_2O$$
$$2H\ CO_2CH_3 = HCHO + CO_2 + (CH_3)_2O$$

With titania we have a third set of products:

$$CH_3CO_2C_2H_5 = CH_3CO_2H + C_2H_4$$
$$2CH_3CO_2CH_3 = 2CH_3CO_2H + C_2H_4$$
$$HCO_2CH_3 = HCO_2H + CH_2 = CO + CH_3OH$$

The decompositions are regular and characteristic with each catalytic agent and the molecules must break or slip at different points in the different cases; but we certainly ought to know what the hypothetical intermediate stages are.[1] Take the case of methyl acetate with nickel, for instance. One assumption might be that we have a methylene dissociation

$$CH_3CO_2CH_3 = CH_3CO_2H + CH_2 = CH_3CH_3 + CO_2$$

A second assumption is that methyl splits off:

$$CH_3CO_2CH_3 = CH_3CO_2 + CH_3 = C_2H_6 + CO_2$$

A third assumption might be a splitting off of both methyl groups:

$$CH_3CO_2CH_3 = 2CH_3 + CO_2 = C_2H_6 + O_2.$$

Is any of these what happens and how can we prove it? Also how does the final assumption tie in with the facts that in aqueous solution acetate ion goes to ethane and CO_2

$$2CH_3CO_2 = C_2H_6 + 2CO_2$$

and that dry lead tetra-acetate decomposes at about 140° into lead acetate, methyl acetate and carbon dioxide

$$Pb(CH_3CO_2)_4 = Pb(CH_3CO_2)_2 + CH_3CO_2CH_3 + CO_2$$

The question also comes up as to the changes in the intermediate stages in case the esters are chlorinated more or less completely.

The effect of the catalytic agent is very marked when it comes to the preferential oxidation of mixed gases.[2] At low temperatures, the nature of the catalytic agent may determine which of two combustible gases will burn the more rapidly. In presence of platinum, copper oxide, or chamotte, hydrogen burns more readily than methane, whereas the reverse is true in borosilicate glass bulbs at 300°–400°. Depending on conditions, either hydrogen or carbon monoxide will burn the more readily.[3]

[1] This is now being studied experimentally by Professor Homer Adkins.

[2] Henry: Phil. Mag., **65,** 269 (1825); Bone: Jour. Chem. Soc., **81,** 535 (1902); **85,** 694 (1894); Proc. Roy. Inst., **19,** 82 (1908); Phil. Trans. **215,** 298 (1915).

[3] Rideal: Jour. Chem. Soc., **115,** 993 (1919).

At very high temperatures the specific effect of the catalytic agent becomes negligible because the reaction will take place so rapidly in the gas phase.

One very striking characteristic of solid catalytic agents is the ease with which they become inactive or are poisoned. Since the reaction takes place in or at the surface, it follows that any substance which cuts down the rate at which the reacting substances reach the catalytic surface[1] or which prevents them from reaching it, will decrease the reaction velocity and may destroy the catalytic action entirely. Berliner[2] has shown that traces of fatty vapors from the air or from the grease on the stop-cocks will decrease the adsorption of hydrogen by palladium from nearly nine hundred volumes practically to nothing. Faraday[3] has shown that traces of grease destroy the catalytic action of platinum on oxyhydrogen gas. De Hemptinne[4] has apparently shown that carbon monoxide cuts down the adsorption of hydrogen by palladium, though his method of presenting his results is very obscure. Lunge and Harbeck[5] found that carbon monoxide inhibits practically completely the catalytic action of platinum on a mixture of ethylene and hydrogen. Schönbein[6] pointed out that the hydrides of sulphur, tellurium, selenium, phosphorus, arsenic, and antimony act very energetically in cutting down the catalytic action of platinum on mixtures of air with hydrogen or ether. He considered that the hydride must decompose, giving rise to a solid film. This is not necessary in order to account for the phenomenon; but he seems to have been right in at least one case, for Maxted[7] has found that hydrogen sulphide is decomposed by platinum black with evolution of hydrogen and that the platinum then does not adsorb hydrogen. Langmuir[8] believes that oxygen prevents the dissociation of hydrogen by a heated tungsten filament because it cuts down the adsorption of the hydrogen.

[1] Taylor: Trans. Am. Electrochem. Soc., **36** (1919).
[2] Wied. Ann., **35,** 903 (1888).
[3] Experimental Researches on Electricity, **1,** 185 (1839).
[4] Zeit. phys. Chem., **27,** 249 (1898).
[5] Zeit. anorg. Chem., **16,** 50 (1898).
[6] Jour. prakt. Chem., **29,** 238 (1843).
[7] Jour. Chem. Soc., **115,** 1050 (1919).
[8] Jour. Am. Chem. Soc., **38,** 2272 (1916).

Harned[1] has shown that the rate of adsorption[2] of chloropicrin by a charcoal which has been cleaned by washing with chloropicrin is much greater at first than by a charcoal which has not been so cleaned, although the final equilibrium is apparently about the same in the two cases. This is analogous to the evaporation of water when covered by an oil film. The oil cuts down the rate of evaporation very much but has practically no effect on the partial pressure of water at equilibrium. Taylor points out that normally the time of contact between a gas and the solid catalytic agent is extremely small and consequently anything which decreases the rate of adsorption will cut down the reaction velocity very much.

It is easy to see that the piling up of reaction products[3] will cut down the reaction velocity, if they prevent the reacting substances from coming in contact with the catalytic agent. This has been observed in the contact sulphuric acid process.[4] The explanation that the decrease in the reaction velocity is due to a decreased adsorption of the reacting substances was first given by Fink[5] who is the real pioneer in this line. Although the reaction between carbon monoxide and oxygen is practically irreversible at ordinary temperature, Henry[6] recognized that the presence of the reaction product might slow up the rate of reaction and he proved his point by increasing the reaction velocity when he removed the carbon dioxide with caustic potash. Water vapor checks the catalytic dehydration of ether[7] and of alcohol[8] and hydrogen cuts down the catalytic dehydrogenation of alcohol.

When catalytic poisons are present or are formed during the reaction, the apparent equilibrium may vary with the amount of the catalytic agent. With only a small amount present, the catalytic agent will be poisoned before the reaction has run very far. In the hydrolysis of ethyl butyrate by enzymes, the reaction

[1] Jour. Am. Chem. Soc., **42,** 372 (1020).

[2] Taylor: Trans. Am. Electrochem. Soc., **36** (1919).

[3] Bunsen (1857). Quoted by Deacon: Jour. Chem. Soc., **23,** 736 (1872).

[4] Bodländer and Koppen: Zeit. Elektrochemie, **9,** 566 (1903); Berl: Zeit. anorg. Chem., **44,** 267 (1905).

[5] Bodenstein and Fink: Zeit. phys. Chem., **60,** 61 (1907).

[6] Phil. Mag. (3) **9,** 324 (1836).

[7] Ipatieff: Ber. deutsch. chem. Ges., **37,** 2996 (1904).

[8] Engelder: Jour. Phys. Chem., **21,** 676 (1917).

apparently runs to different end-points, depending on the relative amounts of enzyme.[1] One may also get abnormal end-points in the hydrolysis of a solid, if the product of hydrolysis is also a solid and forms a film over the reacting substance. With one of the war gases, the amount of hydrochloric acid split off in presence of water was practically the same when the amount of water added varied in the ratio of one to four. In other words, an apparent equilibrium was reached at a given concentration of hydrochloric acid in one case and at one-fourth that concentration when four times as much water was added.

The development of some of the technical contact processes has been so interesting that it seems worth while to discuss a few of them briefly, beginning with the contact sulphuric acid process.[2]

Contact Sulphuric Acid Process

In 1831 Phillips discovered that spongy platinum increases the rate at which sulphur dioxide combines with oxygen according to the equation $2SO_2 + O_2 = 2SO_3$. He obtained a patent for this but could not develop a commercial process. In 1846 Jullion patented the use of platinized asbestos. In 1842 Wöhler and Mahla discovered that the oxides of copper, iron, and chromium act like platinum. In the Schroeder-Grillo contact material hydrated magnesium sulphate is soaked in a solution of a platinum salt and then heated in presence of sulphur dioxide. A thin layer of platinum is thus precipitated on the surface of the porous, dehydrated salt, 0.2–0.3 percent of platinum giving an excellent catalytic agent.[3]

Knietsch found that a practically complete conversion of sulphur dioxide into sulphur trioxide could be obtained when sulphur dioxide was diluted with air, the conversion being more nearly complete the greater the ratio of oxygen to sulphur dioxide.

When the experiments were repeated with purified burner gas on a commercial scale, the contact material soon became inert. It was found that this disastrous result was due to impurities in the burner gases. Even when present in apparently negligible

[1] Kastle and Loevenhart: Am. Chem. Jour., **24,** 491 (1900).

[2] Knietsch: Ber. deutsch. chem. Ges., **34,** 4069 (1901).

[3] Rideal and Taylor: Catalysis in Theory and Practice, 86 (1919).

amounts, these impurities play havoc with the catalytic action of the platinum. Arsenic is the most dangerous and next mercury, while antimony, bismuth, lead, iron, zinc, etc., act in so far as they settle on and actually blanket the contact material. An amount of arsenic equal to 1–2 percent of the platinum in the contact material will destroy the catalytic action completely. In view of the enormous volumes of gas which are handled, it is easy to see to what an infinitesimal value the arsenic content must be reduced.

By cooling the burner gases slowly and bringing them into intimate contact with sulphuric acid, it was found possible to obtain a gas mixture which passed all ordinary optical and chemical tests and which appeared to be pure. When tested on the large scale, it was still found to contain arsenic. The gases had been cooled in long iron tubes and had reacted with these sufficiently to give traces of arsine. This difficulty was eliminated by not letting the gases come in contact with the iron. When the roaster furnaces were run to maximum capacity, however, a slight cloud was formed which could not be got rid of and which proved to consist of unburned sulphur. This in itself would have done no harm had not the particles of sulphur contained some arsenic. It therefore proved necessary to admit enough air so as to be sure that the sulphur was burned completely. While no one has shown that the presence of arsenic cuts down the adsorption by platinum, it is quite certain from Berliner's experiments on palladium and hydrogen[1] that this must be the case.

In American practice the burner gases carry arsenic, lead sulphate, silicon tetrafluoride, hydrochloric acid, sulphur, and selenium. Reese[2] calls the first two permanent poisons and the others temporary poisons. When working with platinum on a magnesium sulphate base, it is possible to regenerate the contact material after it has been poisoned with arsenic by heating with hydrochloric acid. The assumption was that the arsenic was volatilized as the trichloride. Analysis showed, however, that there might be 2–3 percent of arsenic in the regenerated catalyst without its having any apparent effect. It must be that the

[1] Berliner: Wied. Ann., **35,** 804 (1888).

[2] Jour. Soc. Chem. Ind., **22,** 351 (1903).

arsenic had agglomerated in some way so that it did not coat the platinum. In spite of Knietsch's statement to the contrary, it is possible to filter out all the solid poisons.

Under ordinary conditions sulphur dioxide and oxygen combine very slowly and sulphur trioxide dissociates very slowly in the absence of catalytic agents. In presence of catalytic agents sulphur trioxide begins to dissociate perceptibly at about 400° and is practically completely dissociated at 1000°. At first sight it would therefore seem that the process should be run below 400°. The time factor is a complicating one, however. With platinum as catalytic agent the reaction begins at about 200°, but is relatively slow at that temperature, and under commercial conditions there is practically no reaction below 400°. It has proved best technically to work at about 425°–450°, the increased reaction velocity compensating for the decreased chemical efficiency. At 425° the conversion is 98 percent, dropping to 91 percent at 500°. Ferric oxide can be used as a catalytic agent; but the reaction velocity is less and consequently it is necessary to work at a higher temperature with a correspondingly lower chemical efficiency, perhaps 60 percent. Ferric oxide is much less susceptible to arsenic poisoning than is platinum, presumably because of the higher temperature at which it acts. Since arsenic oxide is itself a catalytic agent when free from iron,[1] there must be temperatures at which it will have little or no deleterious action. If one could make a ferric oxide catalyst which would work at as low a temperature as platinum, it is probable that it would be about as sensitive to arsenic poisoning as platinum. It is entirely a question of the way in which the arsenic precipitates on the surface of the catalytic agent.

The heat of reaction for the conversion of sulphur dioxide into sulphur trioxide is given as 22,600 cal per mol of gaseous sulphur trioxide. Since this heat is evolved at the surface of the contact material, it is quite a serious matter to keep the temperature within the proper range. The technical manufacture of sulphur trioxide is therefore very largely an engineering problem and the recent improvements have been chiefly changes in design[2] so as to give more efficient temperature control.

[1] Cf. Berl: Zeit. anorg. Chem., **44**, 267 (1905).

[2] Zeisberg: Trans. Am. Electrochem. Soc., **36** (1919).

Hargreaves Salt-cake Process

The Hargreaves and Robinson process[1] for making salt-cake was established on a practical basis in 1870. The upper temperature limit is about 600° owing to the fusion of the salt. Originally the process involved no catalytic agent but consisted simply in the passage of pyrites gases over suitably prepared salt at 500°–550°, the reaction being

$$4NaCl + 2SO_2 + O_2 + 2H_2O = 2Na_2SO_4 + 4HCl$$

In 1886 small amounts of iron oxide were added as a catalytic agent. Krutwig[2] showed that without ferric oxide about 28 percent of the sulphur in pyrites was converted into sodium sulphate after four hours at a red heat. With ferric oxide a 70 percent yield was obtained at high temperatures and 90 percent at lower ones. The action is also accelerated by cupric oxide and, since 1907, 0.1–1.0 percent of copper or iron salts or both have been added to the salt before the latter is moulded, the amount added depending on the required purity of the product. When the salt-cake is to be used in glass works, only a small amount of the catalytic agent can be added; but the maximum amount is permissible when the salt-cake is intended for the LeBlanc soda process. Increasing the amount of catalytic agent increases the reaction velocity and lowers the temperature at which the action starts. In this particular process there is little or no difficulty with the poisoning of the catalytic agent because the oxides are not used over and over again.

Deacon Chlorine Process

In 1845 Oxland[3] discovered that chlorine is formed to some extent when a mixture of hydrochloric acid and oxygen is passed over a heated porous substance. The reaction is $4\ HCl + O_2 = 2H_2O + 2Cl_2$; but the reaction does not proceed fast enough to be

[1] Thorpe: Dictionary of Applied Chemistry, **5**, 25 (1913); Jobling: Catalysis and its Industrial Applications, 32 (1916); Rideal and Taylor: Catalysis in Theory and Practice, 89 (1919).

[2] Recueil Trav. chim. Pays-Bas, **16**, 173 (1897).

[3] Thorpe: Dictionary of Applied Chemistry, **2**, 18 (1918); Jobling: Catalysis and its Industrial Applications, 26 (1916); Rideal and Taylor: Catalysis in Theory and Practice, 99 (1919).

practicable commercially. In 1855 Vogel treated cupric chloride alternately with hydrochloric acid and oxygen. In 1888 Deacon and Hurter put the process on a successful technical basis by passing a mixture of hydrochloric acid and oxygen over pumice impregnated with cupric chloride which acts as a catalytic agent. It is usually assumed that this is not a case of adsorption catalysis but that the cupric chloride breaks up into chlorine and cuprous chloride which latter combines with oxygen to form cupric oxychloride, $CuO.CuCl_2$. This reacts with hydrochloric acid to form cupric chloride, after which the whole series of reactions take place again and again. There is no real proof of this[1] and it is really quite as probable that the oxygen does react direct with the hydrochloric acid,which is what it must do when there is no cupric chloride present. The catalytic agent is very sensitive to the effect of impurities, such as sulphur dioxide, sulphur trioxide, and arsenic. It is because of this sensitiveness to sulphur dioxide that the hydrochloric acid from the Hargreaves salt-cake process cannot be used in the Deacon process. Water is also bad for the reaction. The gases are therefore dried at 40° before entering the decomposer, as it is called. The temperature at which the best results are obtained is about 450°–460°. Above this temperature the cupric chloride volatilizes too rapidly and at lower temperatures the reaction velocity is too low. About two-thirds of the hydrochloric acid is converted into chlorine.

Chance-Claus Process

In the LeBlanc process for making sodium carbonate, calcium sulphide is a by-product. As far back as 1837 Gossage[2] patented a process for using this tank waste. His plan was to treat the calcium sulphide with carbon dioxide and then to burn the resulting hydrogen sulphide to sulphur according to the equations,

$$CaS + H_2O + CO_2 = CaCO_3 + H_2S$$
$$2H_2S + O_2 = 2S + 2H_2O$$

Gossage failed because he could not get a sufficiently concentrated CO_2 to start with or a sufficiently concentrated hydrogen sulphide for the second stage of the process. This problem was solved by Chance in 1887.

[1] Hurter: Jour. Soc. Chem. Ind. **2**, 106 (1883).

[2] Jobling: Catalysis and its Industrial Applications, 33 (1916).

The burning of the hydrogen sulphide was carried out according to a process patented by Claus but developed further by Chance.[1] The Claus kiln consists of a cylinder provided internally with a grating upon which rests a layer of broken fire-brick, with a further layer of bog-iron ore superimposed. The combustible mixture enters at the top, passes through the porous layers, where it is burned to sulphur vapor and steam with but little sulphur dioxide and sulphuretted hydrogen as impurity, and is drawn from the bottom into a series of condensing chambers, where part of the sulphur vapor condenses to liquid sulphur and the remainder as flowers of sulphur along with the condensed steam. The reaction is exothermic, so that no external heating is necessary. To start the reaction, a few shovelfuls of red-hot coal are thrown on to the oxide; whilst the temperature is regulated by controlling the speed of the gas. During the process the ferric oxide becomes transformed into pyrites, but the pyrites so formed has some peculiar property attached to it which ordinary pyrites do not possess, for the latter is quite useless as a catalyst. When once the necessary temperature has been reached, the reaction is found to proceed fairly satisfactorily with other contact material such as broken brick, though the working temperature then becomes somewhat higher than when ferric oxide only is employed. For starting the reaction, however, ferric oxide or similar contact material must be employed; hence the two layers in the Claus kiln.

Salamon[2] says that the ferric oxide undergoes no change. If that is so, it is not necessary to account for the difference in behavior between natural pyrites and that formed in the Claus kiln. If iron sulphide is actually formed, the alleged difference in behavior is undoubtedly due to a difference in surface and consequently of adsorption. The natural pyrites is of course only very slightly porous. Rideal and Taylor[3] consider that the reaction takes place in two stages,

$$Fe_2O_3 + 3H_2S = 2Fe\,S + 3H_2O + S$$
$$4FeS + 3O_2 = 2FeO + 4S.$$

They do not discuss the behavior of natural pyrites.

[1] Jobling: Catalysis and its Industrial Applications, 33, (1916).
[2] Thorpe: Dictionary of Applied Chemistry, **5**, 294 (1917).
[3] Catalysis in Theory and Practice, 112 (1919).

Haber Ammonia Process

In the contact sulphuric acid process it was found that sulphur trioxide dissociates practically completely into sulphur dioxide and oxygen, at 1000°, while recombination is practically complete at 400° if equilibrium is reached. Matters are not so favorable in the case of the synthesis of ammonia from nitrogen and hydrogen. At 1000° ammonia is practically completely dissociated just as is sulphur trioxide; but at 550° the theoretical amount of recombination at atmospheric pressure is about 0.08 percent instead of 100 percent. Increase of pressure displaces the equilibrium so that more is formed of the system occupying the lesser volume, namely ammonia. At 550° and 200 atm. the amount of ammonia formed is almost 12 percent. The data[1] are given in Table XVIII.

Table XVIII.—Equilibrium Data for Ammonia Synthesis

Reaction is $N_2 + 3H_2 = 2NH_3$

Pressure in atm.	550°	650°	750°	850°	1000°
	Percentage ammonia				
1	0.077	0.032	0.916	0.008	0.006
100	0.7	3.02	1.54	0.87	0.54
200	11.9	5.71	2.99	1.68	1.07

Though the yield of 12 percent is low, the ammonia can be removed as ammonia of crystallization by ammonium nitrate at low temperatures,[2] a fresh supply of the reacting gases can be added to the unchanged nitrogen and hydrogen, and the whole can be passed repeatedly through the reacting chamber until the concentration of methane and argon becomes too high.[3] What catalytic agent to use is a question of first importance. The first catalytic agents tried were nickel, manganese, iron and chromium; afterwards experiments were made with osmium and

[1] Haber: Jour. Soc. Chem. Ind., **33**, 53 (1914).

[2] Thorpe: Outlines of Industrial Chemistry, 151 (1916).

[3] Rideal and Taylor: Catalysis in Theory and Practice, 241 (1919).

uranium.[1] While metallic osmium and uranium carbide are apparently the best for laboratory work, they are not well adapted for technical use.[2] Judging by the most recent patents, pure iron[3] is the catalyst generally employed in this process. Using this material and with the aid of various minor improvements, it is said to be found possible to lower the working pressure to the neighborhood of 50 atmospheres. In all cases, it is essential in the interests of efficiency, that the catalyst be prepared at a temperature not greatly exceeding 600°. Of the remaining substances which catalyze the reaction, the most interesting are molybdenum and molybdates, tungsten and its alloys, and cerium with its congeners. Platinum, on the other hand, though related to osmium, possesses but a slight catalytic activity. It was found that the activity of the catalysts can be increased by the addition of certain foreign bodies. These "promoters," as they have been called, include various metals, the oxides, hydroxides, and salts of the alkali and alkaline earth metals, as well as many other substances of the most varied nature. In many cases just a trace of the contaminating body enhances considerably the activity of the catalyst. Moreover, all the catalysts appear to possess the capacity for invigoration.[4] There are no data to show whether these so-called promoters change the degree of adsorption of any of the substances concerned in the reaction or whether they prevent a possible sintering of the catalytic agent. Mannich and Thiel[5] state that charcoal increases the adsorbing power of palladium for hydrogen. Rideal and Taylor[6] consider that the promoters may cause the relative adsorption of the reacting substances to approach the theoretical ratios more closely.

The contact ammonia process is very susceptible to poisons. Among the harmful substances are sulphur, selenium, tellurium, phosphorus, arsenic, boron, and their compounds; many carbon compounds; lead, zinc, bismuth, tin, etc.[7] Such minute quanti-

[1] Haber: Jour. Soc. Chem. Ind., **33,** 54 (1914).
[2] Jobling: Catalysis and its Industrial Applications, 42 (1916).
[3] Cf. Jellinek: Zeit. anorg. Chem., **71,** 121 (1911).
[4] Pease and Taylor: Jour. Phys. Chem. **24,** 241 (1920).
[5] Jour. Soc. Chem. Ind., **35,** 548 (1916).
[6] Catalysis in Theory and Practice, 29 (1919).
[7] Jobling: Catalysis and its Industrial Applications, 44 (1916).

ties of any of the above-mentioned substances as are to be found almost always in the purest commercial products and so-called pure gases are sufficient to diminish the catalytic efficiency very seriously. For instance, an impurity of 0.01 percent sulphur in iron renders it nearly useless. The Haber process was of enormous value to the Germans during the war.

Ostwald Nitric Acid Process

In 1830 Kugelmann[1] observed that ammonia can be oxidized to nitric acid in presence of platinum. About eighty years later the process was put on a semi-commercial basis by Ostwald. The nominal reaction may be written $NH_3 + 2O_2 = HNO_3 + H_2O$; but the real reaction is the formation of nitric oxide, which is then oxidized to nitrogen peroxide, and afterwards converted into nitric acid,

$$4NH_3 + 7O_2 = 4NO + 6H_2O + 2O_2 = 4NO_2 + 6H_2O = 2HNO_3 + 2HNO_2 + 4H_2O$$

The problem is complicated by the apparently simultaneous oxidation to nitrogen, a reaction which is usually written

$$4NH_3 + 3O_2 = 2N_2 + 6H_2O$$

It is more likely that the disturbing reaction is an oxidation of ammonia by nitric oxide,[2] perhaps

$$4NH_3 + 6NO = 5N_2 + 6H_2O.$$

Both the reactions are accelerated by platinum; but, fortunately, the reaction yielding nitric oxide takes place much more rapidly than the reaction giving rise to nitrogen. The best results are obtained by keeping the gases in contact with the catalytic agent for as short a time as possible, which is an argument for the reaction producing nitrogen being a secondary one. If the two reactions took place simultaneously, the ratio of the two sets of products should be independent of the rate of passage of the gaseous mixture. A mixture of ammonia with ten or more volumes of air is passed at a velocity of 1–5 meters per second

[1] Jobling: Catalysis and its Industrial Applications, 45 (1916).
[2] Sabatier and Senderens: Comptes rendus, **135**, 278 (1902).

through a plug of platinum gauze, 1–2 cm in length and kept at 300°. This gives a period of contact not exceeding 0.01 sec. Under favorable conditions an 85 percent conversion of ammonia is claimed. Better results have been obtained in this country,[1] with several layers of platinum gauze,[2] the yield running 92 percent, with a flow of 250 cubic feet per minute. The average concentration of ammonia is 10.7 percent. A smooth platinum gauze is not effective. After some time it becomes roughened and activated. Contrary to what Ostwald had believed, a high temperature, say above 825°, is better than a lower one. Phosphine is a bad poison, having a distinct effect even when present three parts per hundred million, but cyanogen compounds are not bad because they oxidize readily. Iron oxide, grease, oil or tar must be kept away from the platinum gauze and a new gauze should be washed with pure gasolene or ether before being activated. Ammonia from any source can be used though Landis[3] claims that the platinum must be activated anew when changing to a different ammonia.

Sabatier's Hydrogenation Process

Sabatier and Senderens[4] discovered, a number of years ago, that reduced nickel will cause hydrogen to combine with ethylene or acetylene forming ethane. This has since developed into a general hydrogenation process.[5] The principle of the method is a simple one. The vapor of the substance to be reduced is mixed with hydrogen and passed directly over specific metallic catalysts maintained at temperatures usually held between 150° and 300°. The process is extremely rapid, since complete hydrogenation occurs during the short time the mixture is passing over the catalyst. Rapidity, however, is not the only advantage, for Sabatier and his collaborators, Senderens, Mailhe, and others, who have worked on this method for some fifteen years, find it to be one which, whilst requiring the minimum of attention, furnishes very high yields.

[1] Parsons: Jour. Ind. Eng. Chem. **11,** 541 (1919).

[2] Perley: Jour. Ind. Eng. Chem. **12,** 5, 119 (1920).

[3] Trans. Am. Electrochem. Soc., **35,** 300 (1919).

[4] Comptes rendus, **124,** 1358 (1897); **128,** 1173 (1899).

[5] Jobling: Catalysis and its Industrial Applications, 68 (1916); Sabatier: Die Katalyse in der organischen Chemie, 44 (1914).

The metals which are suitable as catalysts are nickel, cobalt, platinum, iron and copper, of which nickel is far and away the most active, while the others are arranged in diminishing activity. As would be anticipated, the practicability of the method depends largely upon the condition in which the metal is used. It must be prepared by reduction of the oxide, the activity depending upon the nature of the oxide employed and the temperature at which it is reduced. In general the greater the surface exposed the greater the activity, so that the conditions must be carefully arranged to satisfy this requirement. Reduction at a low temperature is found to yield a metal which is too active and too sensitive to external influences, while reduction at a high temperature reduces the catalytic action almost to zero. Consequently, a suitable intermediate temperature must be chosen. Sabatier finds that the best nickel for the purpose is produced by dissolving the metal in nitric acid, calcining the nitrate at a dull red heat, and then reducing the oxide slowly at a temperature of about 300°–325°, until water is no longer evolved. After the nickel has been prepared as described, it is necessary to keep it out of contact with the air, as it is extremely pyrophoric and quickly loses its activity on exposure.

Weight for weight, the efficiency of pure nickel is not so great as that which has had its active surface increased by the aid of some suitable carrier. Hence many proposals have been made for combining the catalyst with a great variety of supporting bodies, ranging from pumice and kieselguhr to charcoal and sawdust.

The materials used, whether hydrogen, metal, or organic compound, must be as pure as can be obtained, for any impurity is readily adsorbed by the catalyst to the detriment of its activity. Sulphur and its volatile compounds, as well as the halogens,[1] are particularly to be avoided in this respect, and, to a lesser degree, arsenic and phosphorus with their volatile compounds. Electrolytic hydrogen, or hydrogen of equivalent purity, appears to be essential. Even then the catalyst must, sooner or later, succumb to the toxic effects of minute impurities impossible to remove; in consequence, the desirability of frequent renewals needs emphasis.

[1] The nickel oxide must not be prepared from the chloride because of the great difficulty of washing out the last traces of adsorbed chloride.

Of practical importance is the preparation of numerous artificial perfumes by the aid of this reaction. Moreover, it permits of the production of cyclohexanol and *p*-methyl cyclohexanol, easily obtained from phenol and *p*-cresol respectively, which are used in the manufacture of isoprene and butadiene, and seem, therefore, destined to play an important part in the synthesis of rubber.

Probably the most important technical application of Sabatier's hydrogenation process is to the conversion of liquid and unsaturated fatty acids such as oleic acid[1] into solid and saturated acids such as stearic acid. As the acid is not vaporized, this process does not belong strictly speaking under the general head of gas reactions accelerated by solid catalytic agents, so I merely refer to it because it is a further development of the same principle.

Sabatier's Dehydrogenation Process

Attention has already been drawn to the fact that alcohols may split off hydrogen or water at a given temperature, depending on the nature of the catalytic agent. Finely divided metals,[2] such as copper, cobalt, nickel, iron, platinum, and palladium catalyze almost exclusively the dehydrogenation process. So also do some anhydrous oxides, chief among which are the lower oxides of manganese, tin, uranium, molybdenum, vanadium, and cadmium, though the activity of these is less than that of the metals. The dehydrogenation of alcohols, both primary and secondary, is most readily effected by reduced copper. If a fatty alcohol be passed over this catalyst at 200°–300°, a yield of at least 50 percent aldehyde or ketone can usually be condensed.

Cyclic alcohols may be dehydrogenated in a similar way. Borneol, for instance, can be transformed into camphor by passage over reduced copper at 150°, whilst geraniol under similar conditions gives citral. The former fact is utilized industrially in the treatment of certain camphors which are sold very cheaply

[1] Cf. Ellis: Jour. Soc. Chem. Ind., **31**, 1155 (1912); Shaw: Ibid., **33**, 771 (1914); Ellis: Jour. Ind. Eng. Chem., **8**, 886 (1916); Ellis: The Hydrogenation of Oils, 2nd Ed., 108 (1918).

[2] Jobling: Catalysis and its Industrial Applications, 82 (1916).

on account of their large content of borneol. As the usual process for removing borneol by means of nitric acid is very slow and unsatisfactory, the above dehydrogenation method, which yields nearly pure camphor, has found ready application in this field.

Of the other catalysts, cobalt, iron, platinum, as well as the above-mentioned oxides, are less advantageous. Zinc is stated to possess high activity. Nickel is ruled out on account of the violence of its reaction, for it pushes decomposition too far.

The most important of the industrial applications of this reaction is the preparation of formaldehyde from methyl alcohol.[1] The earliest recorded production of formaldehyde is to be found in the classic experiment of Hofmann's (1867), in which a red-hot coil of platinum wire suspended over methyl alcohol in a beaker continued to glow there so long as it is in contact with a mixture of the vapor and air. This method forms the basis of most of the subsequent attempts and of the present commercial process. Air is driven through wood spirit kept at a temperature suitable for saturation and the mixture then passed into the catalyzer, usually copper gauze.

In the so-called oxidation of methyl alcohol, the primary reaction is the splitting-off of hydrogen[2] and the practically simultaneous depolarization by oxygen,

$$2CH_2OH + O_2 = 2HCHO + 4H + O_2 = 2HCHO + 2H_2O.$$

Hofmann[3] found that osmium tetroxide oxidizes alcohol to aldehyde but not to acetic acid, acting apparently as a carrier for oxygen. It is probable that we have here a catalytic splitting of the alcohol, the nascent hydrogen reacting with the osmium tetroxide. Wieland[4] considers that the contact sulphuric acid process really involves a dehydrogenation, the reactions being:

$$SO_2 + H_2O = H_2SO_3$$
$$H_2SO_3 = SO_3 + H_2$$
$$2H_2 + O_2 = 2H_2O$$

[1] THORPE: Dictionary of Applied Chemistry, **2,** 592 (1912).
[2] LEBLANC and PLASCHKE: Zeit. Elektrochemie, **17,** 47 (1911).
[3] Ber. deutsch. chem. Ges. **46,** 1657, 2854 (1913).
[4] Ibid. **45,** 685 (1912).

Surface Combustion

The subject of surface combustion has been developed by Bone in England[1] and by Lucke in America. Bone began by a study of the combination of hydrogen and oxygen in contact with hot surfaces of porcelain, magnesia, silver, gold, platinum, nickel, calcined spathic iron ore (containing 79.0 percent ferric oxide and 14.5 percent manganous oxide), nickelous oxide, and copper oxide. With each of these surfaces the rate is proportional to the pressure of the dry gas when electrolytic gas is used, is approximately proportional to the partial pressure of hydrogen when either gas is present in excess, and is increased by a previous treatment with hydrogen. In the case of porcelain, Bone decides that porous porcelain occludes or condenses both hydrogen and oxygen at rates which depend to some extent upon the physical condition and past history of the surface. While the process is extremely rapid in the case of oxygen and the surface layer is soon saturated, the occlusion of hydrogen is slower and the limit of saturation much higher. Combination between the occluded gases occurs at a rate either comparable with, or somewhat faster than, the rate at which the film of occluded oxygen is renewed, but considerably faster than the rate of occlusion of hydrogen.

In later papers Bone[2] showed that all incandescent substances are capable of accelerating gaseous combustion; and to an approximately equal degree, for the wide differences between the catalytic powers of various surfaces at low temperatures gradually diminish as the temperature rises, until at incandescence they practically disappear. If an explosive mixture of a combustible gas and air is pressed through the pores of a granular, high-melting solid, and if the issuing gas be lighted, it will speedily raise the granular solid to incandescence if the conditions are right, after which the heated surface will accelerate the rate of combustion so much that the whole of the gas will be burned at the surface of the solid and we shall have what has been called flameless combustion. As a matter of fact there is flame, but the flame is so short and the light from the incandescent solid so intense that there seems to be no flame. The combustion

[1] Phil. Trans., **206A**, 1 (1906); Jour. Franklin Inst., **173**, 101 (1912).

[2] Summarized in Ber. deutsch. chem. Ges., **46**, 5 (1913); Jobling: Catalysis and its Industrial Applications, 51 (1916).

takes place only at the surface layer of the granular solid but all over the surface and not as flames between each solid particle. The advantages of this surface combustion are an intense and a localized heat, combustion with minimum excess of air, and the development of a large amount of the heat as radiant energy. By passing the explosive mixture through a porous diaphragm we get an incandescent surface which can, if need be, be held glowing side down over a solution which is to be evaporated. In this way, it is possible, for instance, to evaporate a water-glass solution without danger of bumping. The sodium silicate forms as a solid film on the surface of the solution and can be removed from time to time. This form of heating has proved very successful in making candy.[1]

The granular mass may be piled in round a crucible or around boiler tubes giving an extremely high efficiency. The maximum temperature depends on the working conditions. The choice of refractory material is determined by the temperatures involved. Under ordinary conditions calcined fire-clay, ganister, etc., are used; but when high temperatures are in question, practically all solids are eliminated except calcined magnesia and carborundum. Attempts are now being made to substitute an atomized liquid fuel for a gaseous fuel. It is stated that the most successful applications of surface combustion to large scale work are where the heat is radiated very quickly so that the temperature of the refractory does not rise unduly—with steam boiler tubes packed in refractory material for instance.[2] Surface combustion furnaces have proved very useful in annealing shell.

Since an explosive gas mixture is used, it is necessary to keep the flame from working back and burning in the mass of the refractory instead of on the surface. Bone does this by regulating the rate of flow of the gaseous mixture. Lucke[3] has described several ways of doing this by special construction of the heater.

Welsbach Gas Mantle

The invention of the gas mantle made it possible for gas to continue to compete with electricity as an illuminant. The

[1] Seager: Jour. Franklin Inst., **177,** 367 (1914).

[2] Reports of Progress of Applied Chemistry, **1917,** 26.

[3] Jour. Ind. Eng. Chem., **5,** 801 (1913).

best results are obtained when the Welsbach gas mantle consists of 99 percent thoria and 1 percent ceria.[1] Pure thoria gives a relatively poor light, but the continuous addition of ceria gradually increases the luminosity to a maximum of ten-fold when 1 percent is present. Any further addition then diminishes the luminosity until, with 10 percent the difference in effect is inappreciable. In present-day manufacture, the cotton, silk or ramie web is impregnated with a 25–33 percent aqueous solution of thorium and cerium nitrates in the proportion of 99:1, together with a little hardening medium, *e.g.*, beryllium nitrate, if necessary.

We are dealing with surface combustion both in the case of the lime light and of the Welsbach mantle, as is shown by the rapid decay of the light of the lime light owing to sintering[2] and the similar though much slower decay of the light of the Welsbach mantle. Mantles of magnesia and lanthana give a good light when new; but the light decreases as the surface becomes glassy. While a thoria mantle reaches a high temperature,[3] its emissive power is low. Ceria has a high emissive power in the visible spectrum; but the energy of radiation is so great that the temperature of a ceria mantle does not rise high enough. Starting with thoria and increasing the amount of ceria increases the emissive power but lowers the temperature of the mantle. The maximum luminous efficiency is obtained when the rise of visible emission due to the ceria is balanced by the drop in the temperature of the mantle due to the increased radiation. The ceria may form a solid solution with the thoria but there seem to be no data to show whether equilibrium is actually reached in the mantle.

[1] Jobling: Catalysis and its Industrial Applications, 62 (1916).

[2] Steinmetz: Radiation, Light and Illumination, 92 (1909).

[3] Ives, Kingsbury and Karrer: Jour. Franklin Inst., **186**, 401, 585 (1918).

CHAPTER II

ADSORPTION OF VAPOR BY LIQUID AND OF LIQUID AND SOLID BY SOLID AND LIQUID

Adsorption of Vapor by Liquid

Campbell[1] believes that one source of error in the method of determining molecular weights by the so-called air-bubbling method is due to the formation of a film of adsorbed air on the surface of the solution which interferes with the evaporation. He deduced the existence of an adsorbed gas film from his quantitative measurements on evaporation. The existence of such a film is shown directly by Rayleigh's experiments on liquid jets.[2] A vertical jet of water or any liquid slows up and breaks into drops when the head is sufficiently great relatively to the diameter of the jet. These drops scatter because they rebound when they strike one another. If a feebly electrified body is brought close to the jet, the jet becomes coherent. Under more powerful electrical action the scattering of the drops becomes even greater than when there is no electrification. What happens is that there is formed round each drop a film of adsorbed air which prevents two drops from coalescing when they collide. When the drops are electrified, the air film is removed to such an extent that the drops come more nearly in contact and coalesce. With higher electrification, a marked charging of the drops takes place and the repulsion of the like charges causes the drops to scatter. Nipher[3] states that drops of 1 mm radius do not attract each other when charged to 0.0031 volt. That there is an air film between the drops can also be shown by letting two jets impinge under such conditions that they bound apart. It was found that whenever the jets rebounded, the electrical insulation was practically perfect. Rayleigh found that presence of dust

[1] Trans. Faraday Soc., **10,** 197 (1915).

[2] Rayleigh: Proc. Roy. Soc., **28,** 406; **29,** 71 (1879); **34,** 130 (1882).

[3] Science, **34,** 442 (1911).

or addition of a drop of milk had a marked effect on the ease with which the drops coalesce. The reason for this has not been worked out.

In Worthington's experiments on splashes[1] the adsorbed air film plays an important part. A drop of water may fall on a sheet of water in such a way that the drop passes below the surface, becoming completely submerged, and then emerges at the head of a column of adherent liquid with the upper portion apparently unwetted by the liquid with which it has been covered. When the water drops from an oar on the recover, we often get what are known as rolling drops[2] which depend on the presence of adsorbed air films and which are also sensitive to the presence of electrified substances.

If the surface of a sheet of water is covered with oil or with a scum of oily soot or of plankton organisms, a mist or fog may deposit drops on the surface which will be extremely persistent. This phenomenon is not at all uncommon at Lake Mendota at Madison and has frequently been observed elsewhere.[3]

Since soap-bubbles are hollow drops, they should behave in some respects like liquid drops, though not necessarily like drops of a pure liquid. It is possible to press two soap bubbles together with considerable force without causing them to coalesce;[4] but if they are electrified slightly, they coalesce readily without bursting.

It is interesting to note that water will apparently remove a film of adsorbed air much more readily from a polished surface of ivory or marble than it will from a water surface;[5] but we do not know whether this is true for all solids. Sakulka[6] obtained somewhat different results with lead shot, but this may have been because they were not polished.

If a vapor is adsorbed by a liquid, it will condense to a liquid film at a temperature above that of the normal dew-point. Can-

[1] Worthington: Proc. Roy. Soc., **34,** 217 (1882).

[2] Osborne Reynolds: Chem. News, **44,** 211 (1881); Kaiser: Wied. Ann., **53,** 681 (1894).

[3] Juday: U. S. Monthly Weather Review, **44,** 65 (1916); Nakamura: Jour. Meteorological Soc., Japan, **36** (1917).

[4] Boys: Phil. Mag. **25,** 409 (1888).

[5] Worthington: Proc. Roy. Soc., **34,** 217 (1882).

[6] Drude's Ann., **25,** 892 (1908).

tor[1] realized this with water and mercury and Clark[2] with olive oil which is not a well-defined and reproducible liquid.

Adsorption of Liquid by Solid

If a liquid is adsorbed at a solid surface, it forms a liquid film and we say that it wets the solid. If a liquid is not adsorbed by a solid, it does not wet the latter. There has been a good deal of question whether the liquid meets the wall at a definite angle, the contact angle, or whether the contact angle is zero. Lord Rayleigh[3] states definitely that in his opinion the contact angle is zero,[4] and this must be true if we consider that the liquid is adsorbed by the solid. The formation of a liquid film over the surface of a wetted solid accounts for the generally accepted fact that the rise of a liquid in a capillary tube is independent of the nature of the walls of the tube. This has always seemed a very improbable state of things and one that could only be justified by the fact that it was so. The whole thing becomes quite simple when we consider that the rising liquid does not come in contact with the walls of the capillary tube at all.[5] We are really dealing with the rise of a liquid in a liquid tube and it makes no difference what material is used to support the walls of the liquid tube. That this is the real explanation may be seen from the fact that concordant results are not obtained when a liquid is allowed to rise in a dry tube. To get good results it is important to immerse the tube in the liquid and then to raise it. Bigelow and Hunter[6] claim that the nature of the walls does have an effect on the capillary rise; but their experiments were not done in a capillary tube.

On the assumption that the contact angle is zero, a thin film of liquid must rise to the top of the tube, irrespective of the height and diameter of the tube. This has been recognized explicitly by Lord Rayleigh.[7] When the liquid does not wet the solid,

[1] Wied. Ann., **56,** 492 (1895).
[2] Proc. Am. Acad., **41,** 361 (1906).
[3] Scientific Papers, **3,** 393 (1902).
[4] Cf. Harkins and Brown: Jour. Am. Chem. Soc., **41,** 522 (1919).
[5] Rayleigh: Scientific Papers, **3,** 421 (1902).
[6] Jour. Phys. Chem., **15,** 367 (1911).
[7] Scientific Papers, **3,** 523 (1902).

mercury and glass for instance, the assumption of a zero contact angle leads to at least one awkward conclusion. The upper part of the meniscus is certainly not in contact with the glass and therefore none of the mercury is in contact with the glass. If we have a glass tube, infinitely long, closed at the bottom, and filled with mercury, we must conclude, if we are going to be strictly logical, that the column of mercury does not touch the glass at any point and that it stands alone, surrounded on all sides by a film of air, mercury vapor, or something which is not glass. Personally, I feel no desire to be so logical as that. It seems to me probable that at some point the force of gravity squeezes out all the vapor layer and that the mercury does come in contact with the glass. This is the more certain because we know that the mercury sometimes tends to hang in a freshly-made barometer and this could not happen if the mercury were not in contact with the glass.

For a liquid to wet a solid in the presence of air, the liquid must be adsorbed more strongly than the air and must displace it. Hofmann[1] gives a number of details as to the slowness with which some liquids displace adsorbed air from certain solids. In some cases heating is necessary to get quick results. Lycopodium powder is distinctly difficult to wet. Gum arabic adsorbs air strongly and is not wetted readily by water. If ground with alcohol, the alcohol displaces the air and then the gum is wetted more easily by water. The floating of metallic powders or of pieces of metal on water is due to the slowness with which water wets them. The Cape Cod lighter consists of a porous stone set in a brass handle. When this is dipped into a can of kerosene, the kerosene is sucked rapidly into the pores displacing the air. The light is taken out, lighted, and placed under the logs of a wood fire. The adsorbed kerosene burns for about ten minutes, enabling one to do away with paper and even kindling wood. Another interesting application of the adsorption of a liquid by a solid is the case of solidified bromine.[2] It consists of siliceous earth saturated with bromine, which can be driven out by heat.

Of more technical importance is the adsorption of fused magne-

[1] Zeit. phys. Chem., **83,** 385 (1913).

[2] Brand: Zeit. anal. Chem., **26,** 222; Jour. Chem. Soc., **52,** 688 (1887). Cf. Thorp: Outlines of Industrial Chemistry, 251 (1916).

tite by chromite.[1] The simple form of magnetite arc consists of a lower, negative, magnetite terminal and an upper non-consuming terminal of copper, of such size that it does not get so hot as to oxidize or evaporate, but sufficiently hot to avoid condensation of magnetite vapor. When the arc is struck, a pool of melted magnetite forms on the surface of the magnetite terminal and the arc-conductor issues from a depression in this melted pool. The straight magnetite arc flickers badly; but this can be overcome by mixing the magnetite with some more refractory material, such as chromite. The chromite remains solid and holds the melted magnetite as a sponge does water. In this way, these arcs have been made steady and thereby suitable for industrial use.

We are quite familiar with the fact that glass must be cleaned before it can be wetted satisfactorily by water; but it is not so well known that platinum is only wetted by mercury under special conditions.[2] "Mercury, which holds even a very little sodium in solution, has the power of wetting platinum in a very remarkable manner. The appearance of the platinum is quite similar to that presented by amalgamable metals in contact with mercury. But the platinum is in no wise attacked. Further, the amalgam may be washed off by clean mercury, and the latter will also continue to adhere closely to the platinum. All the phenomena of capillarity are presented between the two. The surface of the mercury in a platinum cup so prepared is quite concave; and a basin of mercury may be emptied if a few strips of similarly prepared platinum foil be laid over its edge—just as a basin of water may be emptied by strips of paper or cloth, and under the same condition, namely that the external limb of such capillary siphon be longer than the internal one. The sodium removes the oxide film and permits the mercury to come in contact with the platinum."

It is found that iron, copper, bismuth, and antimony are also wetted by mercury if their surfaces are first touched with sodium amalgam.

A few years later a technical application of this observation was made. Kirchman[3] reports that sodium amalgam can be

[1] Steinmetz: Radiation, Light, and Illumination, 110 (1909).

[2] Guthrie: Proc. Roy. Soc., **13,** 458 (1864).

[3] Jour. Chem. Soc., **26,** 418 (1873).

used advantageously in simplifying the method of dry-gilding iron. Surfaces of iron and similar metals, even though oxidized, are immediately amalgamated by simply rubbing with amalgam. Gold chloride in concentrated solution is then applied quickly on the amalgamated surface, and the mercury volatilized by the heat of lamp or fire. A very uniform gilding is thus obtained, permitting a high polish. Corresponding results are obtained with silver and platinum salts.

Wald[1] has pointed out that there must be a lowering of the vapor pressure of a liquid, when a liquid wets a solid. Consequently, if water really wets ice, or if water rises in a capillary tube made of ice, the vapor pressure of dry ice will differ from that of wetted ice at the same temperature. This point is not taken into account in books on the phase rule because effects due to capillarity, gravity, etc., are usually ruled out explicitly.

The adsorption of a liquid film may introduce quite an error in the determination of the specific gravity of bodies when they are weighed in a highly divided state. As long ago as 1848 Rose[2] pointed out that platinum in the state of foil has a specific gravity between 21 and 22 while a value above 26 was found for platinum precipitated from the chloride by sodium carbonate and sugar. Similar though less extreme differences were found with gold, silver, and barium sulphate. This can be accounted for if we assume that the powder is not weighed alone in water but in conjunction with a film of condensed water.[3]

It was Edward Lear who wrote about the Jumblies who went to sea in a sieve. He considered that a nonsense rhyme; but modern science is almost equal to the problem, for we can carry water in a sieve. If we take a fine-meshed metal sieve and oil the meshes, air can still pass readily through the holes; but water does not wet the wires and consequently surface tension prevents it from passing through the holes.[4] Gasolene may be freed from water by filtering through a 200 mesh metal sieve. We can carry water in such a sieve[5] if we do not fill it too full;

[1] Zeit. phys. Chem., **7,** 514 (1891).

[2] Pogg. Ann., **73,** 1 (1848); Jour. Chem. Soc., **1,** 182 (1849).

[3] See however Johnston and Adams: Jour. Am. Chem. Soc., **34,** 563 (1912).

[4] Chwolson: Lehrbuch der Physik, **1** III, 613 (1907).

[5] Campbell: Jour. Ind. Eng. Chem., **6,** 762 (1919).

but an oiled sieve is not a perfect substitute for a pail. This principle has received an important technical application in the shower-proofing of textile fabrics.[1] The fibers are coated with some water-repellent hydrocarbon, wax, or salt, in which case the fabric will be porous to air but will shed water up to a certain point.

All campers are familiar with the unpleasant fact that a tent will leak in a rain if one touches the canvas with one's finger. The tent is shower-proof and not water-proof. When one pushes against the tent, it either contracts or expands the air spaces. If the air spaces contract, air is driven out and when the finger is taken away, water enters. If the air spaces expand, water runs in. Either way the air is displaced at that point and water enters. What happens can best be seen from an analogy. If one dips a fountain pen filler into ink and presses the bulb, air is driven out and ink enters when the pressure is relieved. If one pinches the bulb before dipping the glass end into the ink, no air bubbles out but ink goes in as soon as the pressure is taken off. It makes no difference therefore whether one touches a tent from the inside or the outside. In either case, water is drawn into the pores of the fabric and the tent leaks continuously once the air is displaced. Awnings on a boat usually leak where they rest on a wooden or iron support. This is because there is always enough wind or vibration to be equivalent to the touching of the tent with the finger. For the same reason, a tent is apt to leak around the pole.

The reverse case is to be seen in the ordinary water wings. They are made of a fine-meshed fabric which is first thoroughly wetted so that a film of water is formed in the pores. The strength of this water film is so great relatively that one can blow up the water wings without the air escaping and the water wings will support a grown person without difficulty.

Ehrenberg and Schultze[2] point out that many powders, when once thoroughly dried, are not easy to wet. After a period of drought, drops of rain will often roll along the dust without wetting it. Even in the case of a shower the dust may be only wetted to a depth of less than a quarter of an inch. This is

[1] C. O. Weber: Jour. Soc. Dyers and Colourists, **17,** 146 (1901).

[2] Zeit. Kolloidchemie, **15,** 183 (1914).

shown by Ehrenberg and Schultze to be due to the adsorbed air on the surface of the solid. Any treatment which cuts down the amount of adsorbed air makes the dust, or soot, or other substance, more easily wetted.

It is not easy to wet carbon black with water; but if the oily material is driven out by a preliminary treatment with superheated steam, carbon black is dispersed by water very rapidly and the liquid bubbles like soda water owing to the escape of the adsorbed air. If a 50 cc vessel is filled with good cocoanut charcoal and if water is then added until the vessel is full up to the mark, 150–200 cc of air will be driven off.

A case analogous to that of the oiled sieve holding water has been described by Lord Rayleigh[1] who found that a piece of iron gauze pressed down upon the flat bottom of a glass vessel, holding a shallow layer of mercury, remained on the bottom of the vessel and did not rise through the mercury. It is quite clear from this that one could carry mercury in an iron sieve. With sodium in the mercury the amalgam would run through the gauze. Rayleigh's experiment of course would not succeed if tried with sodium amalgam instead of with mercury.

Since the adsorption of liquids by solids is selective, it follows that one liquid will be adsorbed more by a solid than will a second liquid and that consequently the first will displace the second from contact with the solid. No systematic study of this phenomenon seems to have been made; but we know that kerosene will displace water in contact with copper and that water will displace kerosene in contact with quartz,[2] while alcohol will displace oil in contact with metal[3] and linseed oil[4] will displace water in contact with white lead. According to this, one should use a rag dipped in alcohol with which to wipe off a lamp and it is for this reason that we cover metal surfaces with vaseline or with a heavy oil to prevent rusting. Parkerized or phosphatized iron is said to owe its non-rusting properties to an oil film. In the kitchen, people wet the moulds before putting in corn starch or gelatine, and they butter the pans before making fudge, or grease

[1] Scientific Papers, **4**, 430 (1903).
[2] Hofmann: Zeit. phys. Chem., **83**, 385 (1913).
[3] Pockels: Wied. Ann., **67**, 669 (1899).
[4] Cruickshank Smith: The Manufacture of Paint, 92 (1915).

the griddles before making flapjacks. It is claimed that aluminum griddles do not need to be greased because the air in the oxide film keeps the cakes from sticking; but the same reasoning ought to apply to frying-pans when used for the same purpose and apparently does not. In making pottery, it is the practice to oil the dies when making dust-pressed ware.[1] Infusorial earth is excellent[2] for cleaning glass plates for photographic purposes. Even very greasy plates become clean very rapidly when rubbed with infusorial earth moistened with water. Some of the methods of removing grease spots from clothes depend on selective adsorption.[3]

There are almost no quantitative data on selective adsorption. Graham[4] made a few rough measurements on the selective adsorption of liquids by palladium. A piece of foil was immersed in a liquid for an hour and afterwards dried by pressure for a few seconds between folds of blotting paper. One thousand parts of palladium foil were found to retain 1.18 of water, 5.5 of alcohol, 1.7 of ether, 0.54 of acetone, 4.5 of gylcerine, 3.5 of benzene, 10.2 of castor oil, and 18.1 of oil of sweet almonds. Quite recently Mathers[5] has shown that lead adsorbs certain essential oils from aqueous solution.

Since the adsorption is selective, a vapor or liquid will be adsorbed more readily by one surface than by another. A striking application of this is to be found in the old daguerreotype process. The latent image is formed on a plate of silver coated with silver iodide and it is developed by means of mercury vapor. The mercury condenses on the places which have been exposed to light. I have seen a patched cement cellar floor on which moisture condensed so markedly on the weathered portion that it seemed as though a pipe had broken under the floor.

If the adsorption is very marked we may get intense strains.[6] Gelatine is adsorbed so strongly by glass that the gelatine film on drying will often tear off the surface of the glass. On the other

[1] Simcoe and Smith: Trans. Am. Ceramic. Soc., **14,** 558, 567 (1912).
[2] Koller: The Utilization of Waste Products, 310 (1915).
[3] Lake: Jour. Phys. Chem., **20,** 761 (1916).
[4] Jour. Chem. Soc., **20,** 275 (1867).
[5] Trans. Am. Electrochem. Soc., **31,** 271 (1917).
[6] Graham: Jour. Chem. Soc., **17,** 320 (1864).

hand, it does not adhere to plates of mica or calcite. With agar-agar we get a state of things which appears to vary with the concentrations. Certain agar-agar jellies will adhere readily to glass while others apparently do not. People have claimed that the substitution of agar-agar for gelatine in photographic plates would be impossible on a technical scale, because the agar-agar film would slip off if the plates were set vertically to dry; but it is probable that this difficulty would be overcome if that were the only drawback.

The whole theory of adhesives depends in part on the fact that the cementing material adheres strongly to the two surfaces and hardens there. It is therefore possible that one agglutinant may be useful for a number of different materials, such as wood, glass, metal, ivory, etc., while others give good results only with special materials. Since the books give different recipes for cements for glass, cements for metals, cements for metals and glass, etc., the differences in adsorption are real ones though no one has ever made a careful study of agglutinants from this point of view.

A good glue joint in wood will easily stand a strain of 6000 lbs. per square inch. We are quite familiar with this; but we do not always realize that the tensile strength of liquid water is pretty high if a decrease in the cross-section can be prevented. As far back as 1850 Berthelot[1] filled a glass tube nearly full of liquid, removed the air, sealed the tube, heated the tube until it was entirely full of liquid, and allowed the whole thing to cool. The liquid continued to fill the tube until the volume was larger than it should be for the temperature by 1/420 in the case of water, 1/93 in the case of alcohol, and 1/50 in the case of ether. This indicates a breaking strain of about 50 atm. for water and over 100 atm. for alcohol and ether. Worthington[2] obtained 17 atm. for alcohol. Stefan[3] and Tumlirz[4] consider that the calculated internal pressure of a liquid is a measure of the theoretical tensile strength and they obtain in this way a value for alcohol[5] of about 2000 atm. Some direct measurements of the tensile

[1] Ann. Chim. Phys. (3) **30,** 232 (1850).
[2] Phil. Trans., **183A,** 355 (1892).
[3] Wied. Ann., **29,** 655 (1896).
[4] Sitzungber. Akad. Wiss. Wien., **109** IIa, 837 (1900); **110** IIa, 437 (1901).
[5] Cf. Hulett: Zeit. phys. Chem., **42,** 353 (1903).

strength of liquid films have recently been made by Budgett,[1] who found a maximum breaking strength of about 87 pounds per square inch for steel end-gauges held together by a water film. On the assumption that the water occupied only one-tenth of the surface, this gives a tensile strength of nearly 900 pounds per square inch, or about sixty atmospheres.

Rice[2] reports that certain plastic clays from Montana, when worked in the brick-making machines adhered to iron in a remarkable way whenever they came into contact with that metal. Rice does not explain why these clays should stick to iron. One of the clays was very high in silica, 76.8 percent.

The formation of glazes on pottery and still more of enamels on metals are cases in which the fused or sintered mass must not only adhere to the base after cooling but must also have nearly enough the same coefficient of expansion to prevent the glass or enamel from going to pieces as the temperature changes.[3]

The adsorption of water vapor by gelatine presents some peculiarities. Working in Ostwald's laboratory, von Schroeder[4] found that gelatine contained a thousand percent of water when immersed in liquid water and less than 400 percent when in saturated water vapor at the same temperature. From these and other experiments von Schroeder concluded that the vapor pressure of water in gelatine must be higher than that of pure water, because water distills from the gelatine to the vapor phase. The reason for this unexpected phenomenon is possibly that gelatine has a cellular structure. If a dry paper bag be placed in a space saturated with water vapor, the paper will adsorb a certain amount of water; but there will be little or no tendency for the water to condense inside the bag and fill it with liquid water. If a similar bag is immersed in liquid water, the paper will take up water as before; but water will also pass into the bag and fill it. If the bag is then lifted into the vapor phase, and if the bag is so constructed that the actual dripping is negligible, the water will distill from the curved surface in the bag to the

[1] Proc. Roy. Soc., **82A,** 25 (1912).
[2] Trans. Am. Ceramic Soc., **14,** 610 (1912).
[3] Randau: Enamels and Enamelling, 101 (1912).
[4] Zeit. phys. Chem., **45,** 109 (1903).

plane surface in the containing vessel. The smaller the bag is, the greater will be the curvature of the water within and consequently the higher the vapor pressure. With the microscopic spaces in solidified gelatine, the vapor pressure of the drops of water will be enough higher to counterbalance the difference of levels in von Schroeder's experiments.

While this explanation accounts for the phenomena provided gelatine really has a cellular structure, a point which is not yet generally accepted—it is superfluous if the facts are not as stated. Wolff and Buchner[1] claim that the loss of water when gelatine is placed in the vapor phase is merely due to experimental error.[2] They have certainly shown the possibility of error in von Schroeder's results; but they did no experiments involving as much error as one must assume if von Schroeder's data are worthless. The whole matter is therefore up in the air for the present. Washburn[3] found that moistened clay will dry pretty completely if suspended in a closed vessel above water. He attributes this to the action of gravity. This could only be true in case there were no soluble salts in the clay and in case the pores were so coarse that the capillary rise was not equal to the distance above the water level.

There are other substances which seem to behave like gelatine, though no experiments like von Schroeder's have been performed. Schwalbe[4] states that cotton cellulose takes up 21 percent moisture in presence of saturated water vapor. Masson and Richards[5] find 17.7 percent adsorbed moisture when the vapor phase is 97 percent saturated. By extrapolation to 100 percent this might easily give about 21 percent moisture; but Masson and Richards incline to the view that the curve is asymptotic, in which case the value would be infinite, which seems absurd. Vignon[6] finds that one gram of cotton takes up about five grams of liquid water, while a fine-grained sponge will hold thirty grams of water per gram of sponge, and a coarse-grained sponge

[1] Kon. Akad. Wet. Amsterdam, **17,** May 30 (1914); Zeit. phys. Chem., **89,** 271 (1915),

[2] See also Arisz: Kolloidchemische Beihefte, **7,** 87 (1915).

[3] Jour. Am. Ceramic Soc., **1,** 25 (1918).

[4] Die Chemie der Cellulose, 10 (1911).

[5] Proc. Roy. Soc., **79A,** 421 (1906).

[6] Comptes rendus, **127,** 73 (1898).

only about six grams. Leighton[1] states that absorbent cotton will hold four grams of water when centrifuged at 4000 R.P.M. Some of this water is held in capillary spaces; some is adsorbed on the surface of the cotton; a part is probably dissolved in the cotton; and some may be held in cells. We have no satisfactory way of differentiating between these possibilities.

Dry caseine takes up about 1.25 g water per gram of caseine.[2] Infusorial[3] earth is able to take up more than double its weight of liquid. Wood flour will take up over double its weight of nitroglycerine without running.[4] Fibrous peat, fresh from the bog, may contain 90 percent of water and Sphagnum moss may imbibe as much as two hundred times its own weight of water,[5] which is the reason that this moss is used largely in the trenches for dressing wounds.

If a freshly-broken piece of porous earthenware be pressed against the tongue, water will be sucked up into the pores of the earthenware and the piece will tend to stick to the tongue. When water is drawn up into a capillary space, air is driven out and one at once wonders how much pressure the water will exert under these circumstances. Jamin[6] has made some preliminary experiments along this line. A hole was bored in a piece of dried chalk. Into this hole was dipped one end of a manometer and the hole was then closed. When the chalk was placed in water, the air was displaced from the pores and a pressure of 3–4 atmospheres was obtained. This is not the limiting pressure because the amount of dead space in the manometer was large. A better method would be to determine the pressure necessary for the air to force the water out of the pores of the chalk.

Spring[7] obtained pressures of one-fifth of an atmosphere when water displaced air in contact with sand.

Jamin, Askenasy, and Wiedeburg[8] have described different

[1] Jour. Phys. Chem., **20,** 32 (1916).

[2] Van Slyke and Publow: Science and Practice of Cheese-Making, 179 (1913).

[3] Koller: Utilization of Waste Products, 310 (1915).

[4] Kressman: Met. Chem. Eng., **14,** 372 (1916).

[5] Percy's Metallurgy: Fuel, 208 (1875).

[6] Chwolson: Traité de Physique, **1** III, 622 (1907).

[7] Mem. Soc. belge Geologie, **97,** 13 (1903).

[8] Wied. Ann., **59,** 764 (1896).

forms of apparatus in which water evaporates through a porous tube or a porous cup of plaster into dry air. As the water evaporates off, mercury is drawn up into the tube reaching a height of 90 cm without difficulty. If bubbles of air did not form, water or mercury could be drawn up to incredible heights, limited by the tensile strength of the liquids.

When considering the adsorption of water vapor by cotton, reference was made to the heat developed. Attention might perhaps be called here to Meissner's experiments on the heat developed when powders are wetted by liquids.[1] He found that there was no appreciable difference in the heat evolved when water was taken above and below 4°. His quantitative results were rather discouraging, however, because he found no apparent relation between the amounts of heat evolved and the amounts of powder taken, which must be the result of experimental error. The more careful experiments of Parks[2] showed that when silica, sand or glass is brought in contact with water at approximately constant temperature, the development of heat at 7° is approximately 0.00105 cal. per square centimeter of surface wetted.

Foote and Saxton[3] find that water adsorbed by lamp-black supercools readily to −6° and is not all frozen at −35°. When once frozen, the water does not begin to melt until nearly 0° in the case of lamp-black. Water adsorbed in gelatinous precipitates may start melting at −20°. McIntosh and Edson[4] find that when a salt solution is plunged into liquid air or solid carbon dioxide, the resulting solid forms a constant-melting mixture, melting completely at the temperature at which the solution should have started freezing. It is not clear why this should be so.

Adsorption of Solid by Solid

Dried glue may be considered either as a solid or as a supercooled liquid. If we consider it as a solid, then the adsorption of gelatine by glass is a case of adsorption of a solid by a solid. It is more satisfactory to have cases where there can be no doubt

[1] Meissner: Wied. Ann., **29,** 114 (1886).
[2] Phil. Mag. (6) **4,** 247 (1902).
[3] Jour. Am. Chem. Soc., **38,** 588 (1916); **39,** 627 (1917).
[4] Ibid., **38,** 613 (1916).

but that both substances are solids. We get marked adsorption of rouge by metals.[1] If a metal is polished with rouge which is not kept sufficiently moist, the rouge adheres so firmly to the metal surfaces that it cannot be removed without spoiling the polish. Blue powder is another case of adsorption. Here we have grains of zinc coated with zinc oxide which adheres even when the zinc is melted. Aluminum and nickel are always coated with solid surface films which have marked effects on the properties of the metals. Passive iron owes its peculiar properties to the adsorption and stabilization of a higher oxide,[2] either FeO_2 or FeO_3. It seems probable that vermilion is adsorbed by copper because De la Rue[3] says that electroplated copper blocks cause vermilion to blacken while cast copper does not.

We get what seems to be a case of adsorption of a solid by a solid if we shake a moderately coarse powder with a much finer powder. Instead of the finer powder filling the voids in the space occupied by the coarse powder, the former tends to coat the latter.[4] If the two powders are of different colors, the color of the coarser powder may be masked completely by a relatively small amount of the fine powder. In one experiment 0.032 g of Prussian blue was mixed with 10 g dolomite which passed a 40 mesh sieve and did not pass a 100 mesh sieve. In the second experiment the same amount of Prussian blue was mixed with 10 g dolomite, all of which would pass a 200 mesh sieve. In the the first case, the powder was a deep blue and in the second it was practically white, though the percentage compositions were the same in the two cases. In another experiment 1 percent Fe_2O_3 colored the dolomite a full red when the rouge passed a 200 mesh sieve and the dolomite did not pass a 100 mesh sieve. When the dolomite passed a 200 mesh sieve and the iron oxide did not pass a 100 mesh sieve, the powder was practically white. In a third set of experiments 8 milligrams of lamp-black blackened 10 g dolomite which was coarser than 40 mesh. When the dolomite was ground so that it all passed a 200 mesh sieve, 654

[1] Desch: Metallographie, 210 (1914).
[2] Bennett and Burnham: Jour. Phys. Chem., **21**, 107 (1917).
[3] Mem. Chem. Soc., **2**, 305 (1845).
[4] Fink: Jour. Phys. Chem., **21**, 32 (1917); Briggs: Ibid., **22**, 216 (1918).

milligrams of lamp-black, or over eighty times as much, were needed to produce approximately the same tint.

This behavior of powders is of great importance when using inert fillers in mixed paints.[1] The amount of barytes that can be mixed with colored pigments without injuring them is remarkably large. There are hundreds of brands of para-red paints made and consumed every year by the agricultural implement trade which contain as high as 90 percent of natural barytes. The opacity of paper may be increased by grinding the filler more finely.

Fink has shown that a given mixture of a white non-conducting powder like thoria with a black conducting powder like tungsten may either be black and conduct electricity or white and a non-conductor, depending on the relative coarseness of the two powders. If one strews lycopodium powder over the surface of water and then puts one's finger into the water, the lycopodium powder sticks to the finger and keeps it from being wetted.[2] A coarse powder kept in a bottle will fall to the bottom of the bottle through the force of gravity while a very fine powder will stick to the walls of the bottle discoloring them. Writing on paper with a pencil or on a blackboard with chalk is a phenomenon of about the same type, though the matter is simplified by the roughened surface on which one writes. Solid particles are rubbed off and stick. It seems probable that the possibility of using face powder is merely a special case of a very fine powder adhering to a curved surface.

In phosphate baking powders, the monocalcium phosphate is protected from moisture by an admixture of starch and it is well-known in the trade that the calcium phosphate must not be too fine nor the starch too coarse; potato starch cannot be substituted for corn starch. The retarding effect on the rate of setting of Portland cement, which is produced by the addition of gypsum is probably due to the fact that the finer gypsum powder coats the coarser cement powder and acts to some extent as a protecting film.

In all these cases the powders do not come in actual contact, but are separated by a film of air which, however, holds them

[1] Toch: The Chemistry and Technology of Paints, 113, 138 (1916).

[2] Ehrenberg and Schultze: Zeit. Kolloidchemie, **15**, 183 (1914).

together, thus behaving like a liquid film. Traces of moisture increase the adhesion, as in the case of sugar and blueberries. The fine particles will be held more firmly in hollows in the coarser powders than on projections and will therefore accumulate first in the concave portions, next on the plane surfaces, and last of all on the convex surfaces. Aitken[1] found that hot powders adhered to a cold rod of glass or metal; but fell off when powder and rod were of the same temperature and were repelled when the rod was hotter than the powder. This is due to a lowering of the surface tension of the condensed air film on the hotter side of the powder. It is necessary to work with such coarse particles that they fall off under the influence of gravity except when special conditions prevail.

It has been shown that the time factor is an important one in the wetting of some solids by some liquids, the air film being displaced slowly. It is possible that in some cases adhering powders displace the air film slowly and become really adsorbed by the supporting solid.

Adsorption of Liquid by Liquid

The spreading of one liquid over another is usually considered to depend on the relative surface tensions. If oil is dropped on water, it is assumed that we have a water-air surface, a water-oil surface, and an oil-air surface as shown in Fig. 4. If the surface tension water-air is greater than the sum of the surface tensions oil-water and oil-air, the drop of oil spreads out over the surface of the water. If the water-air surface tension is less than the sum of the other two the oil will draw up into a globule. While this may be a perfectly correct way of looking at things, it is not a useful one because Rayleigh[2] claims that three fluids cannot be in contact simultaneously. The simplest way to look at the

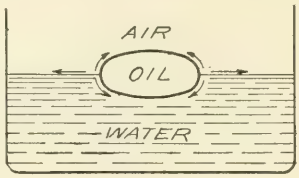


Fig. 4.

[1] Trans. Roy. Soc. Edin., **32**, 239 (1884); Tammann: Drude's Ann., **18**, 856 (1905).

[2] Scientific Papers, **3**, 354, 413, 416 (1902).

matter is to consider the adsorption. If oil is adsorbed by water, it wets the water and spreads over the surface. Now the adsorbed layer may be very thin, not over $2\mu\mu$ in some cases. At greater thicknesses there is nothing to prevent the oil tearing loose from the oiled surface of the water and drawing up into drops under the influence of surface tension. This has been commented on by Rayleigh[1] and by Budgett.[2]

The first portion of oil spreads over the water because it is adsorbed and held by the water. The second portion of oil flows out over the oiled surface, but is instable because the same mass of oil would have a less surface if present in drops and still more so if present in a single drop. The excess oil therefore draws up into one or more drops depending on conditions, thereby leaving bare oiled surfaces. The several drops will coalesce into one large one if brought in contact. If more oil is added the drops become larger and finally form so large a drop that under the influence of gravity, it covers the whole surface of the water and becomes a liquid layer of free oil. From this way of looking at it, we see that the phenomenon must be general and so it is. Budgett[3] found that it was quite impossible to get a thin continuous film of kerosene or water on the surface of steel blocks. Microscopic examination showed that the applied films were not continuous membranes but that the liquid collected into small drops. This is undoubtedly exactly like Rayleigh's experiment. On the surface of the wetted steel the kerosene or water gathered in small drops. With different liquids, we should expect to find the drops first forming when the films reached different thicknesses. This has been noted by Hardy[4] who found that the thickness of the oil film varied from $2–200\mu\mu$ with different oils. With one sample of oil there was apparently no spreading at all.

If an oil is not adsorbed by water, there is theoretically a film of air between the water and the drop of oil. It seems improbable that this air film can continue to exist when a thick layer of oil is present and yet, if not, there must be some point under some

[1] Scientific Papers, **3,** 424 (1902).
[2] Proc. Roy. Soc., **85A,** 30 (1911).
[3] Ibid., **86A,** 30 (1911).
[4] Ibid., **86A,** 612 (1912).

conditions when surfaces of oil, water, and air coexist. It seems probable that Rayleigh's conclusion, that such a state of things cannot exist, holds only when the effect of gravity is ignored. With increasing amount of oil there probably comes a time when the air film is squeezed out entirely. The breaking up of a liquid film into drops has been paralleled by the behavior of thin solid films when heated. Beilby[1] showed that a very thin film of gold leaf became granular if heated moderately.

Adsorption of Solid by Liquid

A solid which is wetted by a liquid, adheres to that liquid. With two liquids and one solid we get selective adsorption of the solid and this leads to some interesting results, which have been studied carefully by Hofmann.[2] If finely divided red lead is shaken with water and benzene or chloroform, the red lead adheres to the surface of the benzene or chloroform, making a practically continuous coating around the organic liquid provided proper relative amounts of red lead and organic liquid are taken. The theory of the phenomenon has been given by Des Coudres.[3] The solid particles tend to go into the water phase if they adsorb water to the practical exclusion of the other liquid; they tend to go into the other liquid phase if they tend to adsorb the other liquid to the practical exclusion of the water; while the particles tend to go into the dineric interface in case the adsorption of the two liquids is sufficiently intense to increase the miscibility of the two liquids very considerably at the surface between solid and liquid.

Of course the powder will only stay in the upper phase or the dineric interface in case it is so fine that the adsorption overbalances gravity. These conclusions as to the way a given pair of liquids will behave with a given solid refer to the relations prevailing under the conditions of the experiment. Hofmann's experiments with two liquid layers in glass test-tubes (soda-lime glass) showed that the time factor might be an important one. If a few cubic centimeters of an aqueous potassium bichromate

[1] Proc. Roy. Soc., **72,** 226 (1904).
[2] Zeit. phys. Chem., **83,** 385 (1913).
[3] Arch. Entwicklungsmechanik, **7,** 325 (1898).

solution are shaken up in a carefully cleaned glass test-tube, there remains on the walls of the test-tube a continuous uniform coating of solution recognizable by its yellow color. This film gradually becomes thinner and paler but does not break at any point until the water disappears completely through evaporation. If one adds a layer of xylene or kerosene to the aqueous bichromate solution in the test-tube, it is easy to see that there is a coating of aqueous solution between the organic liquid and the glass. If water is allowed to flow in at the bottom of the test-tube, the organic liquid can be forced out at the top and there will be no sign of its having adhered to the glass wall at any point. If, however, the test-tube containing the aqueous bichromate solution and the xylene or kerosene be left standing quietly for a long time, 6–10 hours, it will be found that the organic liquid has diffused through the water film to some extent and now adheres to the glass wall nearly everywhere, having displaced the aqueous film almost completely. If the contents of the test-tube are shaken violently, the water displaces the organic liquid from the glass surface practically completely. The glass is therefore wetted more readily and more rapidly by water than by xylene or petroleum; but a large mass of xylene or petroleum will gradually displace a water film from the glass surface. One would therefore expect to get a slightly different behavior with glass powder according as one treated it first with water or with organic liquid. This was exactly what Hofmann found. If the glass powder were treated first with water and then shaken with kerosene, practically all the glass went into the water phase. If the glass powder were allowed to stand a long time with kerosene, or if it were heated with it to hasten the removal of the air film, some of the glass powder would remain in the dineric interface. Vigorous shaking would, of course, cause the water to displace the kerosene. Chloroform behaves towards glass and water somewhat like xylene or kerosene though the tendency to displace the water layer from the glass is less than with kerosene. Small drops of chloroform do not break through the water film at all. With increasing amounts of chloroform the force of gravity causes it to break through at the bottom of the test-tube, the surface wetted by the chloroform increasing as the column of chloroform increases in height.

In Table XIX are given some of Hofmann's results. The letter *w* means that the solid goes nearly completely into the water phase; while *o* denotes that it goes almost completely into the organic liquid; *s* means that the powder collects nearly quantitatively in the interface. Two letters, such as *sw*, mean that the powder goes partly into the interface and somewhat less into the water phase; the use of a parenthesis, *s(w)* or *s(o)*, signifies that there is a good deal more powder in the interface than in the bracketed phase. Benzene and xylene behave alike so only one is given. In the experiments tabulated, the powder was placed in water and then shaken with the organic liquid.

TABLE XIX.—PREFERENTIAL WETTING OF SOLIDS

Water and	Ether	Chloroform	Butyl alcohol	Benzene	Kerosene	Amyl alcohol	Paraffin oil
$CaSO_4$	*w*	*w*	*w*	*w*	*w*	*w*	*w*
SnO_2	*w(s)*	*ws*	*ws*	*s(w)*	*s(w)*	*sw*	*sw*
$Al(OH)_3$	*w(s)*	*ws*	*ws*	*s*	*s(w?)*	*sw*	*s(w)*
SnS	*ws*	*ws*	*ws*	*s(w)*	*s(w)*	*s*	*ws*
$BaSO_4$	*ws*	*ws*	*ws*	*s*	*s*	*s(w?)*	*s(w?)*
ZnS	*w(s)*	*ws*	*ws*	*s*	*s(w?)*	*s*	*s(w?)*
ZnO	*ws*	*ws*	*s(w)*	*s*	*s*	*s*	*s*
$CaCO_3$	*ws*	*ws*	*s*	*s*	*s*	*s*	*s*
$Mg(OH)_2$	*s(w?)*	*ws*	*s*	*s*	*s*	*s(w)*	*sw*
Al	*sw*	*s(w)*	*s(w)*	*s*	*s*	*s(w)*	*s*
$BaCO_3$	*ws*	*ws*	*s*	*s*	*s*	*sw*	*s*
CuS	*ws*	*s(w)*	*s*	*s*	*s*	*s*	*s*
$PbCrO_4$	*ws*	*s(w?)*	*s*	*s*	*s*	*s*	*s*
$Cu_2O(?)$	*ws*	*s*	*s*	*s*	*s*	*s*	*s*
MoS_2	*s(w?)*	*s*	*s*	*s*	*s*	*s*	*s*
PbS	*ws*	*s*	*s*	*s*	*s*	*s*	*s*
Fe_3O_4	*ws*	*s*	*s*	*s*	*s*	*s*	*s*
$BaCrO_4$	*ws*	*s*	*s*	*s*	*s*	*s*	*s*
Pb_3O_4	*sw*	*s*	*s*	*s*	*s*	*s*	*s*
C	*sw*	*s*	*s*	*s*	*s*	*s*	*s*
PbI_2	*s*	*s*	*os*	*s*	*s*	*os*	*s*
HgS	*s*	*s*	*s*	*s*	*s*	*s*	*s*
HgO	*s*	*s*	*s*	*s*	*s*	*s*	*s*
HgI_2	*s*	*s*	*s*	*s*	*s*	*o*	*os*
AgI	*s*	*s*	*o*	*s*	*s*	*o*	*os*

Much the same conclusions have been worked out by Reinders[1] independently of Hofmann. Some of his data are given in Table XX. The powder was placed in the water phase and then shaken with the organic liquid.

TABLE XX.—PREFERENTIAL WETTING OF SOLIDS

Water and	Paraffin oil	Amyl alcohol	CCl_4	Benzene	Ether
Kaolin	*w*	*w(s)*	*w(s)*	*w*	*w(s)*
CaF_2	*ws*	*ws*	*w(s)*	*w(s)*	*w(s)*
Gypsum	*w*	*ws*	*w*	*sw*	*ws*
$BaSO_4$	*w(s)*	*ws*	*ws*	*sw-*	*ws*
Magnesium	*ws*	*ws*	*ws*	*ws*	*ws*
PbO	*s*	*s*	*sw*	*s*	*sw*
Malachite	*so*	*s*	*s*	*s*	*sw*
ZnS	*s*	*s*	*s*	*s*	*sw*
PbS	*so*	*so*	*s*	*s*	*s*
HgI_2	*so*	*s*	*s*	*s*	*s*
Carbon	*so*	*s*	*s*	*s*	*s*
Selenium	*so*	*so*	*so*	*s*	*s*
Sulphur	*so*	*so*	*o(s)*	*so*	*s*

Similar results were obtained with colloidal solutions, Isobutyl alcohol was added to a colloidal gold solution obtained by reducing gold chloride with carbon monoxide. When the two liquids are shaken, the gold forms a thin film at the interface. This film is violet blue to blue green by transmitted light and golden by reflected light. A thin water film forms between the isobutyl alcohol and the glass, and the gold concentrates in the dineric interface thus formed, making the alcohol appear uniformly gold-plated. With ether the gold film rises high above the level of the two liquids. With carbon bisulphide the adherent film of gold appears blue. When the carbon bisulphide is broken into drops by shaking, each drop appears blue. When a blue gold was obtained by reducing gold chloride with phosphorus dissolved in ether, the gold went into the dineric interface. When a brownish red gold was obtained in this way, it remained in the water phase and showed no tendency to pass into the interface. This difference is undoubtedly due to an adsorption of something at the

[1] Zeit. Kolloidchemie, **13,** 235 (1913).

surface of the gold because Reinders found that 0.005 percent gum arabic prevents colloidal gold from passing into the ether-water interface. With carbon tetrachloride, carbon bisulphide, and benzene, the gold goes to the interface as before; but the gum arabic prevents its changing from red to blue.

With colloidal ferric oxide practically no iron went into the interface with any of the organic liquids. It seems probable that this is due to Reinders using a ferric oxide solution which was a year and a half old, because hydrous ferric oxide is ordinarily a pretty good emulsifying agent.[1] Colloidal arsenic sulphide goes into the dineric interface with amyl alcohol or butyl alcohol; but stays in the water phase when carbon tetrachloride, benzene, or ether is the second liquid. India ink goes completely into the interface with isobutyl alcohol and stays entirely in the water phase when ether is the second liquid. When crystallized copper eosinate is placed in water and shaken with ether, it goes entirely into the surface between the two layers,[2] giving a film which resembles the purple skin of a grape, by reason of the steel-blue color of the crystals.

An interesting experiment is to shake copper powder or aluminum powder with kerosene and water. The metallic powder goes into the kerosene and into the interface, producing an effect of molten copper or molten aluminum as the case may be. When the bottle is allowed to stand after having been shaken, the metallic powder in the interface creeps up the side of the bottle above the surface of the liquid, rising higher if a little alcohol has been added. I have seen an apparently coherent metallic film rise two or three inches above the surface of the upper liquid phase. If too much copper or aluminum be added the kerosene cannot hold it all up and a portion falls to the bottom of the flask carrying drops of kerosene with it. If the mixture be poured out on a piece of wood, the copper spreads over the surface of the wood just as it did over the surface of the glass. This experiment illustrates the principle involved in all bronzing liquids. A bronzing liquid consists of a volatile liquid which will hold up the metal, and some substance which will keep the metallic powder from rubbing off too readily after it has been applied.

[1] Briggs: Jour. Phys. Chem., **19**, 296 (1915).

[2] Gilbert: Jour. Phys. Chem., **18**, 602 (1914).

The second substance also serves the purpose of keeping the metallic powder in a better state of suspension in the volatile liquid. According to Worden[1] the best of these bronzing liquids consist essentially of pyroxylin dissolved in amyl acetate, to which the metallic powder is added. For bronzing radiators and steam pipes, a pure pyroxylin would not do since it would decompose, disintegrate, and allow the metallic coating to peel off. To prevent this, boiled linseed oil and rosin may be added. Such preparations are of course much slower in drying than pyroxylin bronzing liquids; but that is not a serious objection for these special purposes. A much cheaper form of bronzing liquid consists of rosin dissolved in benzene, while the cheapest of all is apparently a solution of sodium silicate in water. The aluminum and copper powders on the market are coated with stearin; but special experiments in my laboratory have shown that the behavior of copper and aluminum with kerosene is the same qualitatively whether the stearin coating is removed with ether or not.

Barus[2] and Rayleigh[3] have each noticed that when fine powders (bole) or dust are shaken with ether and water the solid particles go into the water layer, leaving the ether layer astonishingly clear. In fact Rayleigh said that the ether layer was more free of motes than he had ever been able to obtain by repeated distillation of liquid in vacuum. White lead passes from water into linseed oil.[4] "During recent years the practice has been adopted largely among white lead corroders who grind their own white lead in oil of doing away with the final drying of the white lead pulp as it comes from the washing process, and grinding or beating up the pulp (exhausted of water until the proportion of the latter does not exceed about 20 percent) with a suitable quantity of refined linseed oil. This process depends on the greater surface attraction which white lead particles offer to linseed oil than to water. It enables considerable economies to be effected in the manufacture of 'ground white lead' and it eliminates risk of lead poisoning during one of the most dangerous

[1] Nitrocellulose Industry, **1,** 310–320 (1911).
[2] Am. Jour. Sci. (3) **37,** 124 (1889).
[3] Scientific Papers, **3,** 569 (1902).
[4] J. Cruickshank Smith: The Manufacture of Paint, 92 (1915).

parts of the white lead manufacturing process." Zinc oxide stays in the water phase. The Elmore bulk-oil process of ore flotation depended on the fact that some sulphide ores can be shaken out of the water phase by means of suitable oils while the gangue stays in the water phase. When ground bituminous coal is stirred up with fuel oil and water, there is a good separation of coal from ash, the former going into the oil and the latter into the water. The readiness with which solid films form over the surface of mercury is well known to everybody. Salts of mercury or of the baser metals coat mercury with great readiness, especially in the air.

CHAPTER III

ADSORPTION FROM SOLUTION

Adsorption from Solution by Solid

Selective adsorption by a solid from a solution may show itself by relatively more of the dissolved substance being adsorbed than of the solvent, or by relatively less being adsorbed. In the first case, commonly called positive adsorption, the solution becomes more dilute and in the second case, commonly called negative adsorption, the solution becomes more concentrated. Both cases are known; but the first one is the more important and will be considered now. The decolorizing action of charcoal[1] has been known since 1791. In 1874 Böttger[2] pointed out that when an alcoholic solution of any of the aniline dyes is shaken up with a sufficient quantity of infusorial earth, some water added, and the whole thrown on a paper filter, the liquid which runs through is perfectly colorless, the pigment being retained by the siliceous earth. The adsorption of dyes by hydrous alumina, stannic oxide, and other mordants as they are called, is of great importance in dyeing. Here as in all other cases the adsorption is selective. Davison[3] showed that when alumina is precipitated from an aluminum acetate solution, it will decolorize dilute solutions of alizarine, alizarine green, benzo orange, and acid violet: it adsorbs fast green, acid green, and croceine orange considerably, and has practically no adsorbing action on emerald green or chrysoidine. Red phosphorus will decolorize a dilute solution of iodine in carbon bisulphide.[4]

Hatschek[5] points out that iodides cannot be shown to be present in sea-water by any of the usual tests, and that we owe our supply of iodine to the adsorption of iodides by certain sea-weeds.

[1] Cf. Ostwald: Lehrbuch allgem. Chemie, 2nd. Ed., **1**, 1093 (1891).
[2] Jour. Chem. Soc., **28** 170 (1875).
[3] Jour. Phys. Chem., **17**, 737 (1913).
[4] Sestini: Gazz. chim. ital., **1**, 323; Jour. Chem. Soc., **24**, 1006 (1871).
[5] An Introduction to the Physics and Chemistry of Colloids, 6 (1913).

When making density determinations[1] by weighing a solid in a solution, an error may be introduced because of the solid adsorbing some of the salt. This error is likely to be larger the finer the particles of the solid, because the ratio of surface to mass increases with increasing subdivision. With grains of quartz or glass varying in diameter from 0.015 mm to 0.9 mm, placed in solutions of iodides, the specific gravity of the latter can be adjusted so that the smaller particles will sink while the larger will float. Marble is so porous that its surface is almost proportional to its volume, and consequently grains of marble do not show this phenomenon.

According to Skey[2] antimony and arsenic can be removed so completely from solutions of their oxides or chlorides in moderately strong hydrochloric acid (with a little tartaric acid in the case of antimony) by charcoal that neither of them can be detected therein by Reinsch's test, although before the treatment they could be detected without difficulty. Commercial sulphuric and hydrochloric acids diluted with a little water can be purified from either of these substances by agitating them intermittently for a short time with fresh charcoal, and then filtering off; application of heat to the mixture expedites this result.

Quite recently Lockemann and Paucke[3] have studied quantitatively the adsorption of arsenic acid by charcoal, hydrous aluminum oxide, hydrous ferric oxide, and albumin. They find that egg albumin and blood serum, when coagulating, carry down certain amounts of arsenic from aqueous solutions. Animal charcoal also adsorbs some amounts of arsenic from aqueous solutions. When hydrous aluminum oxide is precipitated by ammonia, it carries down very appreciable quantities of arsenic. Curiously enough more arsenic is carried down when the hydrous aluminum oxide is precipitated from hot solution than when precipitated from a cold one. This unexpected fact is probably due to the form in which the alumina is precipitated. At the temperature of the water-bath, arsenic in amounts up to 20 mg As per 100 cc can be precipitated completely but this requires the use of very

[1] THOULET: Comptes rendus, **99,** 1072 (1884); Jour. Chem. Soc., **48,** 476 (1885).

[2] Chem. News, **17,** 157 (1868); **36,** 6 (1877).

[3] Zeit. Kolloidchemie, **8,** 273 (1911).

large amounts of alumina. When precipitated by ammonia, hydrous iron oxide carries down large amounts of arsenic, more being carried down the lower the temperature and the smaller the excess of ammonia. When the concentration of arsenic does not exceed 10 mg As per 100 cc it can easily be precipitated quantitatively by means of iron.

In 1845 Yorke[1] discussed the adsorption of lead oxide by filter paper, while Müller[2] and Weiske[3] have shown that filter paper takes up such appreciable quantities of barium, strontium and calcium hydroxides that dilute solutions of these salts should not be filtered if they are to be used for quantitative work.

A special phenomenon in connection with adsorption by filter-paper has been studied by Bayley,[4] Lloyd,[5] Gordon,[6] and others.[7] If a drop of a salt solution be allowed to fall on filter-paper the solution will tend to spread. If the salt is adsorbed very strongly it will not spread and we get a relatively wide water-ring. If the salt is not much adsorbed, it will spread as far as the water. If a strip of filter-paper be dipped into a solution we get a similar phenomenon; the water will rise much farther than the salt if the latter is adsorbed strongly. Gordon found that with a M/40 $CuSO_4$ solution the water rose about 9.2 cm in half an hour and the copper salt only 5.5 cm. With a M/2 solution the copper salt rose 9.2 cm and so did the water. Ordinary ink shows the phenomenon well with blotting-paper.

Leighton[8] has determined the adsorption of caustic soda, hydrochloric acid, sulphuric acid, and phosphoric acid by purified absorbent cotton. These experiments were interesting in two ways. In the first place, they showed that no compounds were formed. In the second place, data were obtained showing the possible error when determining adsorption. The usual method is to shake a known solution with a weighed amount of the adsorbed solid, pipette off some of the supernatant liquid, and

[1] Mem. Chem. Soc., **2,** 399 (1845).
[2] Jour. prakt. Chem., **83,** 384 (1861).
[3] Jour. Chem. Soc., **30,** 662 (1876).
[4] Ibid., **33,** 304 (1878).
[5] Chem. News, **51,** 51 (1885).
[6] Jour. Phys. Chem., **18,** 337 (1914).
[7] See Sahlblom: Kolloidchemische Beihefte, **2,** 79 (1910).
[8] Jour. Phys. Chem., **20,** 188 (1916).

analyze. The amount of adsorption is calculated from the decrease in concentration. This calculation is accurate only in case no liquid is taken up by the solid adsorbing agent. If the cotton adsorbed the alkali and the water in the same ratio in which they occurred in the solution there would be no change in the concentration of the solution and the apparent adsorption would be zero. To avoid this error, Leighton centrifuged the cotton for an hour in a centrifugal rotating about 4000 revolutions per minute, and then analyzed the cotton. This direct or "gravi-

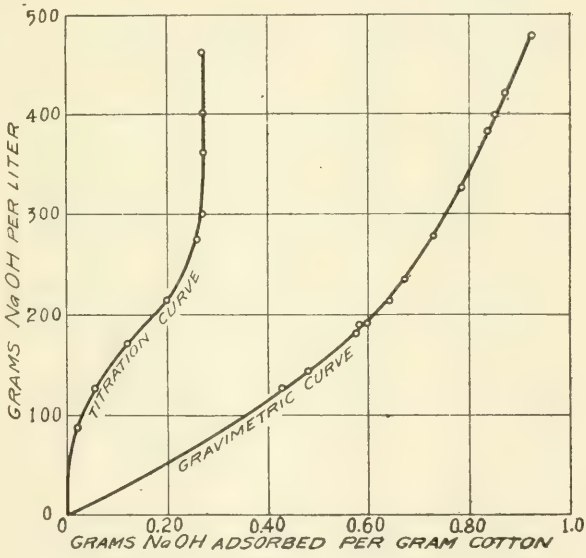


FIG. 5.

metric" method will give too high adsorption unless the centrifuging removes all the unadsorbed solution. On the other hand, the indirect or "titration" method gives too low results unless no water is adsorbed by the cotton at all. Since this last is not true, the results by the titration method are necessarily wrong with cotton, while the results by the gravimetric method may be right. The differences between the two methods may be quite considerable. With a solution of 200 grams NaOH per liter Leighton found an adsorption of 0.27 grams NaOH per gram cotton by the titration method, and of 0.75 gram NaOH by

the gravimetric method. The true adsorption lies between these two values.[1] In Tables XXI–XXIV are given Leighton's data which are also reproduced graphically in Figs. 5–7.

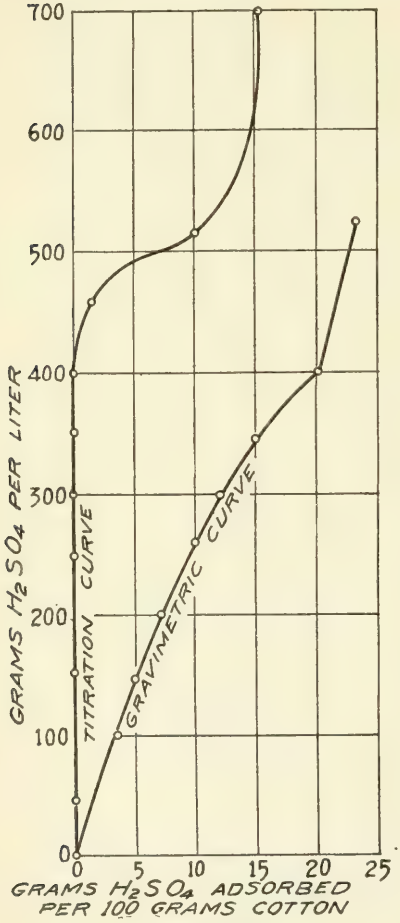


FIG. 6.

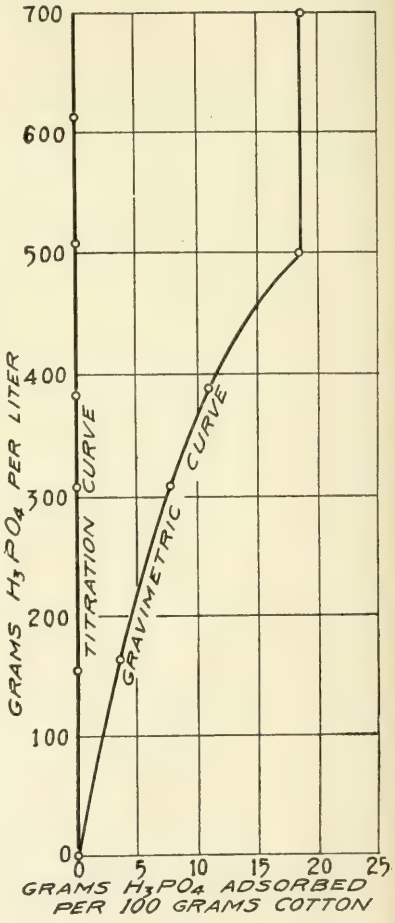


FIG. 7.

Kellner[2] has studied the adsorption of acids and alkalies by platinum black. One gram of platinum black adsorbed about 20 percent of the hydrochloric acid in 50 cc of a thousandth-

[1] See WEISER and SHERRICK: Jour. Phys. Chem., **23**, 205 (1919).

[2] Wied. Ann., **57**, 79 (1895).

TABLE XXI.—ADSORPTION OF SODIUM HYDROXIDE BY COTTON

Volume of solution = 100 cc.
Weight of cotton = about 1.0 g.
Time of run = 3 hours.

Solution grams NaOH per liter	Grams NaOH adsorbed per gram cotton		Solution grams NaOH adsorbed	Grams NaOH adsorbed per gram cotton	
	Gravimetric	Titration		Gravimetric	Titration
474	0.916		230	0.664	
450		0.28	212	0.662	
427	0.887		210		0.19
415	0.875		190	0.594	
400		0.27	189	0.579	
379	0.846		184	0.572	
350		0.27	175		0.12
323	0.782		140		0.08
300		0.27	138	0.461	
276	0.733		125	0.433	
275		0.25	90		0.01
231	0.665		40		0.00

TABLE XXII.—ADSORPTION OF SULPHURIC ACID BY COTTON

Volume of solution = 100 cc.
Weight of cotton about 1.0 g.
Time of run = 3 hours.

Solution g H_2SO_4 per liter	Adsorption	
	Gravimetric: g H_2SO_4 per 100 g cotton	Titration: g H_2SO_4 per 100 g cotton
747.7		2.04
521.7	23.70	1.53
459.2		0.12
413.9	20.99	0.0
352.3	15.36	0.0
302.3	12.55	0.0
252.3	10.00	0.0
202.3	7.35	0.0
151.7	5.77	0.0
101.2	4.65	0.0
50.0		0.0

TABLE XXIII.—ADSORPTION OF PHOSPHORIC ACID BY COTTON

Volume of solution = 100 cc.
Weight of cotton about 1.0 g.
Time of run = 3 hours.

Solution g H_3PO_4 per liter	Adsorption	
	Gravimetric: g H_3PO_4 per 100 g cotton	Titration: g H_3PO_4 per 100 g cotton
715.2	18.68	0
514.4	18.43	0
382.9	11.53	0
318.8	8.57	0
158.0	4.53	0

TABLE XXIV.—ADSORPTION OF HYDROCHLORIC ACID BY COTTON

Volume of solution = 100 cc.
Weight of cotton about 1.0 g.
Time of run = 3 hours.

Solution g HCl per liter	Adsorption	
	Gravimetric: g HCl per 100 g cotton	Titration: g HCl per 100 g cotton
414.0	...	13.97[1]
373.6	9.1	11.63[1]
331.3	7.3	9.28[1]
288.9	6.9	7.00[1]
209.2	6.2	2.34
114.5	3.1	0
45.8	2.0	

normal solution (about 0.36 mg HCl). The adsorption of caustic potash is greater. The bivalent bases and acids are adsorbed in general more than the univalent ones. Osaka[2] has made some experiments on the adsorption of potassium and sodium salts by blood charcoal. The charcoal takes up about 85 percent of its weight of water when suspended in saturated water vapor at 25°. If no account is taken of this fact, a very large error

[1] Probably wrong owing to volatilization of HCl.

[2] Mem. Coll. Sci. Kyoto Univ., **1**, 257 (1915).

may be introduced. When allowance was made for the amount of water adsorbed, it was found that the adsorption with salts of the same base decreased in the order $I > NO_3 > Br > Cl > SO_4$. The results are shown graphically in Fig. 8, the abscissas being milligram equivalents of salt adsorbed per gram charcoal and the ordinates the concentration of the solution in gram equivalents per liter. It will be noticed that potassium salts are adsorbed more strongly than the corresponding sodium salts. The numerical values are given in Table XXV. The percentage adsorptions for normal solutions of KI, KNO_3, KBr, KCl, and K_2SO_4 are approximately 28, 16, 14, 7, and 5 respectively. Rona and Michaelis[1] find that

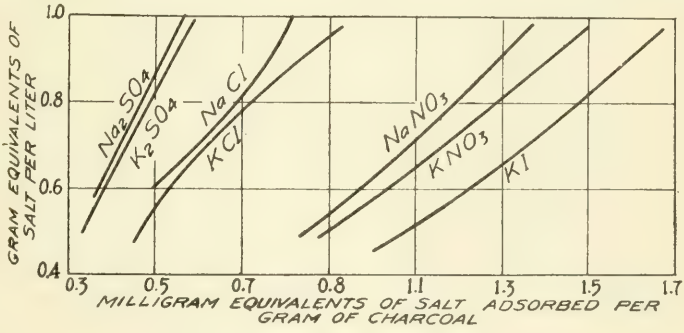


Fig. 8.

the order of adsorption of the anions is $OH > CNS > I > NO_3 > Br > Cl > HPO_4 > SO_4$ and of the cations is $H > Al > Cu > Zn > Mg$, $Ca > NH_4$, K, Na.

With powdered quartz having an estimated surface of 1000 cm^2 per gram, L. J. Briggs[2] found that 100 grams quartz adsorbed approximately the following amounts for M/10 solutions: NaOH, KOH and NH_4OH, 0.8 millimols; Na_2CO_3, K_2CO_3, $(NH_4)_2CO_3$, 0.2 millimols; NH_4Cl, $MgCl_2$, NaCl, $NaNO_3$, Na_2SO_4, nothing.

An interesting and important case of selective adsorption has been worked out by Lloyd. From fuller's earth he has prepared a hydrous aluminum silicate[3] which adsorbs alkaloids. It has been suggested that the material be called Lloyd's reagent.

[1] Biochem. Zeit., **94**, 240 (1919).

[2] Jour. Phys. Chem., **9**, 623 (1905).

[3] Waldbott: Jour. Am. Chem. Soc., **35**, 837 (1913).

TABLE XXV.—ADSORPTION OF SALTS BY BLOOD CHARCOAL

Milligrams and milligram equivalents per gram charcoal

Conc. of solution in g equiv./ liter	Salt adsorbed by one gram charcoal		Conc. of solution in g equiv./ liter	Salt adsorbed by one gram charcoal	
	mg	mg equiv.		mg	mg equiv.
Potassium sulphate			Sodium sulphate		
1.010	51.4	0.59	1.068	40.5	0.57
0.830	45.1	0.52	0.933	37.4	0.53
0.673	37.0	0.42	0.753	31.9	0.45
0.509	29.3	0.34	0.583	25.5	0.36
Potassium chloride			Sodium chloride		
0.966	68.6	0.92	0.998	47.4	0.81
0.765	50.8	0.68	0.896	44.9	0.77
0.562	41.8	0.56	0.697	35.3	0.60
0.470	33.2	0.45	0.597	29.0	0.49
Potassium nitrate			Sodium nitrate		
0.977	151.2	1.50	0.978	116.3	1.37
0.817	129.9	1.28	0.816	107.6	1.27
0.654	112.7	1.11	0.647	99.4	1.03
0.491	87.7	0.87	0.484	69.6	0.82
Potassium iodide			Potassium bromide		
0.967	277.9	1.67	0.970	139.2	1.17
0.833	250.8	1.51	0.717	98.1	0.82
0.622	207.4	1.25	0.526	75.7	0.64
0.464	167.8	1.01			

Carey Lea[1] has shown that silver iodide adsorbs iodine strongly. This property of silver iodide was verified by shaking portions of freshly precipitated and still moist AgI with iodine solutions. An alcoholic solution of iodine, diluted until it has a pale sherry wine color is quickly decolorized by AgI, and the same thing happens with a very dilute solution of iodine in KI, which in a few minutes becomes as colorless as water. It is probably this adsorption which makes silver iodide photographic emulsions apparently less sensitive than the silver bromide emulsions. If so, it should not be difficult to overcome this trouble.

Reinders[2] has found that when silver chloride crystallizes

[1] Am. Jour. Sci. (3), **33**, 492 (1887).

[2] Zeit. phys. Chem., **77**, 696 (1911).

from an ammoniacal solution to which gelatine has been added, the crystals contain adsorbed gelatine. This fact is of great importance for the theory of the photographic emulsion. Much other work on adsorption by crystals is to be found in the papers of Marc.[1] The selective nature of the adsorption is shown by the fact that barium sulphate carries down much larger amounts of barium nitrate than of barium chloride.[2]

In his presidential address before the mathematical and physical section of the British Association, Trouton[3] says: "It is a very well known experiment in adsorption to run a solution such as that of permanganate of potash through a filter of sand, or, better, one of precipitated silica, so as to provide a very large surface. The first of the solution to come through the filter has practically lost all its salt owing to have been adsorbed by the surface of the sand.

"I was interested in finding a few months ago that Defoe, the author of Robinson Crusoe, in one of his other books, depicts a party of African travellers as being saved from thirst in a place where the water was charged with alkali by filtering the water through bags of sand. Whether this is a practical thing or not is doubtful, or even if it has ever been tried; for it is only the first part of the liquid to come through the filter which is purified, and very soon the surface has taken up all the salt it can adsorb and after that, of course, the solution comes through intact. It is interesting, however, to know that so long ago as Defoe's time the phenomenon of adsorption from salt solutions had been observed. It is not so well known, that in the case of some salts under the circumstances mentioned above, the first of the solution to come through the sand filter is stronger instead of weaker. This, as already mentioned, is because water, or at least a weaker solution forms the adsorption layer."

On or just back of the beaches at Galveston, Nantucket, and elsewhere, there are wells of fresh water, the levels of which correspond approximately to the ocean level at high tide. It is often believed that the water in these wells comes from the sea and that the salts have been removed in some mysterious

[1] Zeit. phys. Chem., **61,** 385 (1908); **67,** 470; 68, 104 (1909); **73,** 685 (1910).
[2] Weiser and Sherrick: Jour. Phys. Chem., **23,** 205 (1919).
[3] Brit. Ass. Reports, **84,** 287 (1914).

way.[1] Unfortunately this is not true. The water comes from inland but is backed up by the ocean and does not flow off so rapidly as it otherwise would. If for any reason the outward flow is checked for a sufficient time, the salt from the ocean does work back into the wells. This has been noticed at Galveston when excessive amounts of water are drawn from the wells.

The Adsorption Isotherm

In all cases which have been studied quantitatively the form of the adsorption isotherm is similar to that obtained for the adsorption of gases by solids. Consequently an equation of the same type will represent both sets of phenomena. For solutions we write the equation

$$(x/m)^n = kc$$

where x is the amount adsorbed by m units of the solid adsorbing agent, c is the concentration of the solution, and n is not necessarily an integer though experimentally never less than unity. The approximate accuracy of the formula is shown in Freundlich's data,[2] Tables XXVI—XXVIII. Other adsorption formulas have been proposed or discussed by Freundlich,[3] McBain,[4] Schmidt,[5] von Georgievics,[6] and others;[7] but no formula is strictly accurate and the simplest one seems the best for the time being. If the curve really runs parallel eventually to the axis of ordinates, the simple formula is necessarily wrong.

That this really does happen seems to be shown very conclusively in some experiments by Schmidt[8] on the adsorption of acetic acid by charcoal, Table XXIX. The data are plotted in

[1] Hilgard: Soils, 267 (1906).

[2] Kapillarchemie, 147 (1909); See also von Georgievics: Monatsheft für Chemie, **34,** 733 (1913).

[3] Zeit. phys. Chem., **57,** 385; **59,** 284 (1907).

[4] Jour. Chem. Soc., **91,** 1683 (1910).

[5] Zeit. phys. Chem., **74,** 689 (1910); **77,** 641 (1911); **78,** 667 (1912); **91,** 103 (1916).

[6] Ibid., **83,** 269 (1914).

[7] Marc: Zeit. phys. Chem., **81,** 641 (1913); Dietl: Monatsheft für Chemie, **35,** 784 (1914); Trümpler: Zeit. Kolloidchemie, **15,** 10 (1914).

[8] Zeit. phys. Chem., **77,** 650 (1911).

TABLE XXVI.—DISTRIBUTION OF ACETIC ACID BETWEEN WATER AND BLOOD CHARCOAL

$(x/m)^n = kc$.
$n = 2.35$; $\log k = 0.98$.
c in mols per liter; x/m in millimols per gram charcoal.

c	x/m found	x/m calc.	log k
0.0181	0.467	0.474	0.966
0.0309	0.624	0.623	1.029
0.0616	0.801	0.798	0.984
0.1259	1.11	1.08	1.006
0.2677	1.55	1.49	1.030
0.4711	2.04	1.90	1.055
0.8817	2.48	2.48	0.981
2.785	3.76	4.04	0.906

TABLE XXVII.—DISTRIBUTION OF BROMINE BETWEEN WATER AND BLOOD CHARCOAL

$(x/m)^n = kc$.
$n = 2.4$; $\log k = 0.974$.
c in millimols per liter.
x/m in millimols per gram charcoal.

c	x/m found	x/m calc.	log k
0.92	2.07	2.09	0.965
2.59	3.10	2.96	1.032
6.69	4.27	4.10	1.028
17.08	5.44	5.64	0.930
29.75	6.80	6.80	0.974

TABLE XXVIII.—DISTRIBUTION OF BENZOIC ACID BETWEEN WATER AND BLOOD CHARCOAL

$(x/m)^n = kc$.
$n = 2.53$; $\log k = 2.32$.
c in millimols per liter.
x/m in millimols per gram blood charcoal.

c	x/m found	x/m calc.	log k
6.18	0.437	0.445	2.299
25.00	0.780	0.776	2.329
53.13	1.04	1.04	2.318
117.73	1.44	1.43	2.330

TABLE XXIX.—ADSORPTION OF ACETIC ACID BY CHARCOAL

100 cc acetic acid solution and 10 grams charcoal.
c_1 = grams acetic acid per 100 cc.
c_2 = grams acetic acid adsorbed.

Sugar charcoal		Animal charcoal	
c_1	c_2	c_1	c_2
0.009	0.052	0.04	0.20
0.032	0.101	0.19	0.49
0.037	0.126	1.20	1.19
0.212	0.322	1.88	1.42
1.16	0.588	3.18	1.68
3.76	0.795	5.09	1.96
3.75	0.811	13.63	2.37
5.60	0.828	14.39	2.47
9.18	0.901	21.52	2.56
12.65	0.953	32.06	2.44
16.60	0.904	38.89	2.50
25.73	0.882		
29.38	0.902		
30.60	0.903		

Fig. 9. In both these cases people who only looked at the last five or six figures might easily decide that a definite compound was formed though it would have to be a different one in each case. If one assumes that the animal charcoal is only 20 per cent carbon, the hypothetical compound would be $C_{20}(CH_3CO_2H)$. By assigning a higher molecular weight to carbon, the formula can be made anything one pleases.

Schmidt[1] does not always give the units which he uses and his manipulation of decimal points is erratic; but he finds that the equation

$$(x/m)^4 = kc$$

represents pretty well the distribution of iodine between charcoal and alcohol or benzene over the range covered by the experiments. For charcoal, water, and acetic acid or succinic acid, the equation takes the form

$$(x/m)^2 = kc$$

[1] Zeit. phys. Chem., **15**, 56 (1894).

while the exponent becomes 10 in the case of oxalic acid. For the distribution of potassium chloride between silicic acid and water the exponent is unity, the equation becoming

$$(x/m) = kc$$

The same equation describes the distribution of potassium chloride between stannic oxide and water[1] and between charcoal

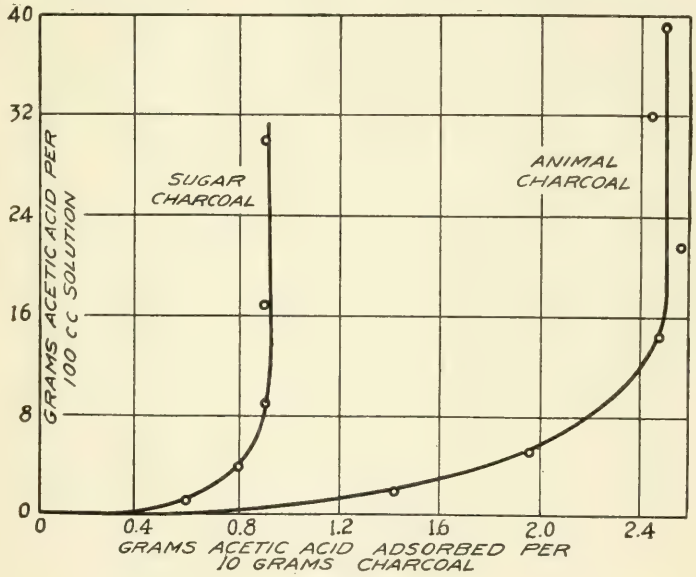


FIG. 9.

and water.[2] A glance at Fig. 8 shows that Osaka's data for potassium sulphate and potassium nitrate fall very nearly on a straight line and could therefore be given approximately by this equation over the range plotted. This has no special significance because the other data in Fig. 8 distinctly do not give straight lines.

Van Slyke and Van Slyke[3] state that the distribution of acids between caseine and water can be represented by the adsorption isotherm, the exponent being 1.95 for sulphuric acid.

[1] VAN BEMMELEN: Zeit. anorg. Chem., **23,** 113 (1900).
[2] LACHS and MICHAELIS: Zeit. Elektrochemie, **17,** 2 (1911).
[3] Am. Chem. Jour., **38,** 383 (1897).

Georgievics[1] finds that the distribution of indigo carmine between silk and water and of methylene blue between cellulose and water can be represented by the formula $(x/m)^2 = kc$, while Küster[2] shows that the distribution of iodine between starch and water can be described by the formula $(x/m)^5 = kc$. Küster's experiments prove that "starch iodide" so-called is not a definite compound. They also furnish a serious objection to the view that the iodine forms a solid solution in starch following the same laws governing the distribution of a substance between two liquid layers. If that were the case the molecular weight of iodine in starch would have to be one-fifth the molecular weight of iodine in water. This means a molecular weight of about 51 for iodine dissolved in starch, which is improbable. This difficulty is avoided when we consider the phenomenon as one of adsorption because there is no known relation between the exponent in the formula for the adsorption isotherm and the molecular weight of anything.

Biltz[3] has shown that the blue color obtained when iodine is taken up by basic lanthanum acetate is due to an adsorption of iodine by the salt. The exponential factor is 2. It is 3 for the distribution of alizarine between chromic oxide and water.[4]

Davis[5] finds that the exponential formula reproduces satisfactorily enough, the data for the distribution of iodine between charcoal and various organic liquids. He considers further that the adsorption of iodine by various charcoals consists of a surface condensation and a diffusion (solid solution) into the interior of the carbon, the surface condensation being nearly instantaneous and quite complete in some hours, while the diffusion proceeds for weeks or months. This conclusion is disputed by Schmidt-Walter,[6] who believes that the charcoal acted as a catalytic agent causing the iodine to react with the organic liquids.

The adsorption of milk sugar and cane sugar by charcoal has

[1] Sitzungsber. Akad. Wiss. Wien., **103,** IIb, 589 (1894); **104,** II*b*, 309 (1895); Zeit. Farbenindustrie, **2,** 253 (1903).

[2] Liebig's Ann., **283,** 364 (1891).

[3] Ber. deutsch. chem. Ges., **37,** 719 (1904).

[4] Biltz: Ber. deutsch. chem. Ges., **38,** 4143 (1905).

[5] Jour. Chem. Soc., **91,** 1666 (1907).

[6] Zeit. Kolloidchemie, **14,** 242 (1914).

been studied quantitatively by Wiegner,[1] the value of the exponent n being about 4.5 for milk sugar and a little less than 8.2 for cane sugar.

Walker and Appleyard[2] have studied the very interesting case of picric acid and silk. The distribution of picric acid between silk and water is reversible and can be represented by the equation $(x/m)^{2.7} = kc$. When picric acid is dissolved in dry benzene, however, dry silk does not adsorb any picric acid from the solution, nor does dry silk, dyed with picric acid, lose any picric acid to dry benzene. It is apparently not a case of reversible equilibrium and Walker and Appleyard were unable to account for it. Quite recently a tentative explanation has been put forward[3] that picric acid, like many other dyes, exists in two forms: in this case the one colored, the other colorless. In water or alcoholic solution the two forms are in equilibrium, and so reversible equilibrium between the liquid and silk exists. But a carbon tetrachloride solution of picric acid, at least at ordinary temperatures and at 60°, contains so little of the colored modification that reversible equilibrium is reached with difficulty. The case of the benzene solution is complicated by presence of the benzene picric acid compound, but this probably has no dyeing properties. One could also prophesy the same results with ligroin or chloroform solutions—in fact with any colorless solution of picric acid. The effect of solvent on tautomeric change is exemplified in the cases of nitroso-benzene and the pseudonitrols, which as solids are colorless, but yield colored solutions.

Cameron and Patten[4] find that the distribution of gentian violet between soils and water or of eosine between quartz and water can be represented fairly well by exponential formulas; but that flocculation of the adsorbing medium is apparently a disturbing factor. That flocculation actually does take place had been shown by Patten[5] in a special set of experiments on quartz flour and dyes.

[1] Zeit. Kolloidchemie, **8,** 126 (1911).

[2] Jour. Chem. Soc., **69,** 1334 (1896).

[3] Blucher and Farnau: Jour. Phys. Chem., **18,** 640 (1914). Cf. Sisley: Bull. Soc. chim., Paris, 865 (1900).

[4] Jour. Phys. Chem., **11,** 581 (1907).

[5] Trans. Am. Electrochem. Soc., **10,** 67 (1906).

In Table XXX are given a list of a few of the systems which have been studied quantitatively. The values for n have undoubtedly been rounded off in most cases.

TABLE XXX.—EXPONENTS IN ADSORPTION ISOTHERMS

Solvent	Solute	Solid	n	Observer
Alcohol	Iodine	Charcoal	4.0	Schmidt[1]
Benzene	Iodine	Charcoal	4.0	Schmidt[1]
Water	Acetic acid	Charcoal	2.0	Schmidt[1]
Water	Succinic acid	Charcoal	2.0	Schmidt[1]
Water	Oxalic acid	Charcoal	10.0	Schmidt[1]
Water	Potassium chloride	Silicic acid	1.0	Schmidt[1]
Water	Potassium chloride	Stannic oxide	1.0	Van Bemmelen[2]
Water	Potassium chloride	Charcoal	1.0	Lachs and Michælis[3]
Water	Sulphuric acid	Caseine	1.95	Van Slyke[4]
Water	Indigo carmine	Silk	2.0	Georgievics[5]
Water	Methylene blue	Cellulose	2.0	Georgievics[5]
Water	Iodine	Starch	5.0	Kuster[6]
Water	Alizarine	Chromic oxide	3.0	Biltz[7]
Water	Milk sugar	Charcoal	4.5	Wagner[8]
Water	Cane sugar	Charcoal	8.2	Wagner[8]
Water	Picric acid	Silk	2.7	Walker and Appleyard[9]

ABNORMAL ADSORPTION

A still more striking case of flocculation and consequent change of adsorption was studied by Lottermoser and Rothe[10] in the

[1] Zeit. phys. Chem., **15,** 56 (1894).
[2] Zeit. anorg. Chem., **23,** 113 (1900).
[3] Zeit. Elektrochemie, **17,** 2 (1911).
[4] Am. Chem. Jour., **38,** 383 (1897).
[5] Sitzungsber. Akad. Wiss. Wien., **103,** 11*b*, 589 (1894); **104** II*b*, 309 (1895); Zeit. Farbenindustrie, **2,** 253 (1903).
[6] Liebig's Ann., **283,** 264 (1891).
[7] Ber. deutsch. chem. Ges., **38,** 4143 (1905).
[8] Zeit. Kolloidchemie, **8,** 126 (1911).
[9] Jour. Chem. Soc., **69,** 1334 (1896).
[10] Zeit. phys. Chem., **62,** 359 (1908).

adsorption of potassium iodide by silver iodide. For concentrations of potassium iodide in water up to about M/300 the exponential formula holds fairly well, the exponential factor being a little over 13. Beyond this concentration the amount of adsorption actually decreases with increasing concentration in the water phase. The change in the structure of the silver iodide can easily be seen under the microscope. The precipitate becomes denser and more granular and shows signs of crystallization. On the other hand silver nitrate is adsorbed by silver iodide without producing this change within the concentrations studied. The exponential factor is 2 for silver nitrate. The silver iodide shows a marked tendency to change in structure and great care is necessary if one wishes to prepare two samples with the same adsorbing power.

Freundlich and Schucht[1] found that amorphous mercuric sulphide changes over spontaneously into a crystalline form and then has a decreased power of adsorbing dyes. The adsorption of eosine by hydrous copper oxide varies with changes in the cupric oxide.[2] Wagner[3] has shown that when the salts of aluminum, iron, etc., are hydrolyzed they adsorb the free acid to some extent; but that in time the adsorption decreases so much that practically all the acid is set free.

Evans[4] reported a number of cases of apparently abnormal adsorption by filter paper. With hydrochloric acid the amount adsorbed was apparently independent of the concentration of the solution from 0.007N to 0.08N. It then increased to double the amount as the concentration of the solution rose to 0.28N and dropped off apparently to zero with 0.36N HCl with normal acid. In a second series the maximum adsorption was found at about 0.2N HCl and there was apparently no adsorption with N/2 acid. A similar behavior was observed with copper sulphate solutions, the maximum adsorption occurring at about 0.04M $CuSO_4$ and the adsorption dropping to zero for a 0.13M solution. The case of hydrochloric acid was studied by Miss Murray[5]

[1] Zeit. phys. Chem., **85,** 660 (1913).
[2] Gilbert: Jour. Phys. Chem., **18,** 592 (1914).
[3] Monatsheft für Chemie, **34,** 95 (1913).
[4] Jour. Phys. Chem., **10,** 290 (1906).
[5] Ibid., **20,** 621 (1916).

who showed that normal results were obtained under ordinary conditions if one titrated with methyl orange as indicator. If one used phenolphthalein as indicator and ignored the presence of carbonate in the standard alkali, abnormal results were obtained. Since the apparently abnormal adsorption in the case of hydrochloric acid was proved to be due to analytical error, it is probable that the measurements with copper sulphate, etc., are not absolutely reliable.

While there is no abnormal adsorption of hydrochloric acid under ordinary conditions, Miss Murray found that the adsorption dropped to less than one-half its original value if filter paper were allowed to stand for 7–10 days in contact with hydrochloric acid solutions. The nature of the change in the filter paper under these conditions is not known. It is also not known whether a similar change is to be observed with purified absorbent cotton.

Biltz and Steiner[1] found abnormal adsorption of night blue and Victoria blue by cotton, the adsorption passing through a maximum with increasing concentration. It is impossible to say to what extent the decreasing adsorption is due to experimental error, to changes in the adsorbing power of the cotton, and to other substances present in the dye-bath.

Negative Adsorption

Lagergren[2] in 1899, reported the negative adsorption of some chlorides and of ammonium bromide by charcoal, the solution becoming more concentrated after being shaken with the charcoal. Quite recently Osaka[3] found that sodium nitrate, potassium bromide, potassium iodide and potassium nitrate are adsorbed positively by blood charcoal while sodium chloride, sodium sulphate and potassium sulphate are apparently adsorbed negatively. The solution of potassium chloride is adsorbed positively when the concentration is comparatively high and is apparently adsorbed negatively when the concentration is comparatively low. With sodium sulphate the increase in concentration was about 1 percent and was less than that with the other salts.

[1] Zeit. Kolloidchemie, **7**, 113 (1910).
[2] Freundlich: Kapillarchemie, 165 (1909).
[3] Mem. Coll. Sci. Kyoto Univ., **1**, 257 (1915).

Mathieu[1] observed negative adsorption with a number of dilute solutions when adsorbed by porous plates, membranes, or capillary tubes. With normal solutions the concentrations in the capillary tubes were often only one-tenth that. The difference in concentration increases with decreasing radius of the capillary tubes and Mathieu considers it quite possible that with very fine tubes water alone would be adsorbed, a conclusion which, as Mathieu himself points out, is of distinct importance for the theory of semi-permeable membranes. If this conclusion is true and general, it accounts for the results of Bigelow[2] and of Bartell[3] who found that osmotic phenomena appeared in porous cups when the pores were sufficiently fine or were clogged sufficiently. It is clear that we can get osmotic phenomena in two distinct ways, depending on whether we have a continuous film or a porous one. In the case of a continuous film, it is essential that the solvent shall dissolve in the membrane and that the solute shall not. Since the permeability is not dependent on adsorption, there is no reason why there should be any fundamental difference between the adsorption of a solute which does pass through the membrane and of one which does not pass through. If we have a porous film, we get osmotic phenomena only in case the pore walls adsorb the pure solvent and the diameter of the pores is so small that the adsorbed film of pure solvent fills the pores full. Under these circumstances the dissolved substance cannot pass through the membrane unless adsorbed by the latter. There is therefore an important difference between a solute which does pass through a porous membrane and one that does not, in that the first is adsorbed by the membrane and the second is not. By making suitable assumptions this distinction can perhaps be eliminated.[4]

Kahlenberg[5] has shown that benzene, toluene, and pyridine pass through a rubber membrane very readily, while water does not. This is perfectly natural on the assumption that these

[1] Drude's Ann., **9**, 340 (1902).

[2] Jour. Am. Chem. Soc., **29**, 1576, 1675 (1907); **31**, 1194 (1909).

[3] Jour. Phys. Chem., **15**, 659 (1911); **16**, 318 (1912); Jour. Am. Chem. Soc., **36**, 646 (1914); **38**, 1029, 1036 (1916).

[4] See Tinker: Proc. Roy. Soc. **92A**, 257 (1915).

[5] Jour. Phys. Chem., **10**, 141 (1906).

liquids dissolve in rubber, but on the basis of pores it is hard to understand why water should not pass through. One might cite the case of the oiled sieve and say that water does not wet rubber, but water does wet rubber. The case of trichloracetic acid is also interesting. When dissolved in benzene it passes readily through a rubber membrane, whereas it passes very slowly when dissolved in water. This is as it should be if we are dealing with solution, but it is hard to explain if we are dealing with adsorption. While nothing is proved, I am inclined to think that a rubber membrane is not a porous one in the sense that Bartell's clogged plate is, and I believe, therefore, that, when a rubber film acts as a semi-permeable membrane, the solvent dissolves in the rubber and passes through it essentially in that way. There are no satisfactory data in regard to the copper ferrocyanide membrane, but it seems better for the present to consider it as like the rubber membrane.

Reversibility of Equilibrium

To be certain that the equilibrium represented by the adsorption isotherm is a reversible one, it should be reached from both sides. As a rule, that is not done, but Freundlich[1] has made a couple of experiments to show that the same end-point is actually reached. For the distribution of acetic acid between charcoal and water, he obtained a concentration in the water of N/16.47 when he shook one gram of charcoal with 100 cc of N/14.53 solution, and a concentration of N/16.49 when he shook one gram of charcoal with 50 cc of a N/7.27 solution and then added 50 cc water. For the distribution of benzoic acid between charcoal and benzene, a similar proceeding with other concentrations gave him the two final values of N/8.5 and N/8.48. In some cases equilibrium is reached very rapidly from both sides, and in others not.[2] While the adsorption equilibrium is theoretically a reversible one, there are conditions under which there may be apparent or actual irreversibility. If charcoal takes a dye out of solution to such an extent as to decolorize the water

[1] Kapillarchemie, 148 (1909); see also von Schroeder: Kolloidchemische Beihefte, **1**, 14 (1909).

[2] Freundlich: Zeit. phys. Chem., **57**, 388 (1906); Ostwald: Lehrbuch allgem. Chemie, **1**, 1096 (1891); Schmidt: Zeit. phys. Chem., **74**, 708 (1910).

practically, no amount of washing with water will give a colored solution, even though dye is being taken out all the time.[1] In this case the adsorption is strictly reversible, and the difficulty was in the interpretation of the results.

There is one experiment which I always like to try, because it proves something whichever way it goes. A solution of iodine in water is shaken with bone-black, filtered, and tested with starch paste. If the colorless solution does not turn the starch blue, the experiment shows how completely charcoal extracts iodine from aqueous solution. If the starch turns blue, the experiment shows that the solution, though apparently colorless, still contains iodine which can be detected by means of the sensitive starch test.

If the adsorbing substance changes through agglomeration, crystallization, or in any other way, its specific adsorbing power will change, and the adsorbed substance will be held either more or less firmly, as the case may be. Some instances of this have already been cited under abnormal adsorption. The adsorbed substance may also change on standing or on heating, in which case we shall have an apparent irreversibility, though we are really dealing, as before, with a new reversible equilibrium. This case occurs very frequently in dyeing.[2]

Specificity of Adsorption

Since adsorption is essentially specific, the amount of adsorption will necessarily vary with the nature of the adsorbing agent, the liquid, and the substance to be adsorbed. In illustration of this, Freundlich[3] cites the experiments of Wöhler, Pluddeman and Wöhler[4] to the effect that charcoal and ferric oxide adsorb benzoic acid about ten times as strongly as acetic acid, while chromium oxide adsorbs the two acids about equally, and platinum black adsorbs acetic acid a little, but benzoic acid practically not at all. All salts seem to show distinct adsorption for their own ions. Thus silver bromide adsorbs silver nitrate or potas-

[1] Freundlich and Neumann: Zeit. phys. Chem., **67,** 538 (1900).
[2] Lake: Jour. Phys. Chem., **20,** 761 (1916).
[3] Kapillarchemie, 155 (1909).
[4] Zeit. phys. Chem., **62,** 664 (1908).

sium bromide, but not potassium nitrate. Charcoal adsorbs both acid and basic dyes. Alumina takes up many acid dyes readily and not the basic dyes; silica and tannin adsorb the basic dyes more readily than acid dyes. Wool adsorbs many dyes strongly without a mordant and cotton relatively few. What is known as Schulze's law[1] is that the power of active ions to precipitate colloidal solutions is a function of their valence, or of the number of electrical charges which they carry. Since the precipitating power, in the cases studied by Schulze, depends on the degree of adsorption, it follows that, in so far as Schulze's law holds, a trivalent ion will be adsorbed more strongly than a bivalent ion, and the latter more strongly than a univalent one. Schulze's law is merely a first approximation. Everybody recognizes that hydrogen and hydroxyl ions are not to be classed with the other univalent ions, because they are usually adsorbed much more strongly,[2] and everybody recognizes that there are other exceptions. In case of doubt, it is generally safe to assume that an ion of higher valence will be adsorbed more strongly than one of lower valence, but it is a mistake to consider this so-called law as anything more than a guide. For instance, Osaka[3] found that charcoal adsorbed potassium salts in the following order when the salts were present in equivalent concentrations: $KI > KNO_3 > KBr > KCl > K_2SO_4$, from which it follows, that, for equivalent concentrations, the sulphate ion is adsorbed the least of all. If we were to compare molecular concentrations the sulphate ion would be adsorbed as strongly as the bromide ion, but less than the nitrate or the iodide ion. Davis[4] found that the order of adsorption of iodine from different liquids was not the same with different kinds of charcoal. With animal charcoal there was decreasing adsorption in the order: chloroform, alcohol, ethyl acetate, benzene, and toluene; with sugar charcoal the adsorption decreased in the order: chloroform, toluene, ethyl acetate, benzene, and alcohol; whereas for cocoanut charcoal the order was toluene, chloroform, benzene, alcohol, and ethyl acetate. There are at least two factors governing the effect of

[1] Schulze: Jour. prakt. Chem. (2) **25,** 43 (1882); **27,** 320 (1884).
[2] Freundlich: Kapillarchemie, 354 (1909).
[3] Osaka: Mem. Coll. Sci., Kyoto, **1,** 267 (1915).
[4] Jour. Chem. Soc., **91,** 1682 (1907).

the solvent. The more soluble the dissolved substance is in a given solvent, the less readily will it be adsorbed, provided we can neglect the adsorption of the solvent itself by the solid. There are many illustrations of this, but one will suffice. Charcoal will decolorize aqueous solutions of iodine or of methyl violet, but alcohol will extract the color from the charcoal. The solubility cannot be the sole factor, however, because then the solvents could always be arranged in the same order for the same solute, regardless of the nature of the adsorbing agent. This is disproved absolutely by the experiments of Davis. One other factor is the adsorption of the solvent by the adsorbing agent. This factor was not taken into account at all by Davis, whose data are therefore not sufficient to enable us to tell whether there are other factors to be considered.

In so far as adsorption is accompanied by an evolution of heat, the amount of adsorption must decrease with rising temperature. This is found to be the case experimentally, but the change is often a very small one. In some cases there is an apparently large increase in adsorption with rising temperature. Thus wool takes up very little acid violet at 20° and a great deal at about 95°. Experiments showed[1] that this adsorption is not reversible, for the acid violet adsorbed at the higher temperature cannot be washed out to any extent at 20°. After adsorption the dye agglomerates or changes so that it becomes practically insoluble and consequently the wool takes up more dye.

Adsorption of Several Solutes

Some years ago there was a widespread rumor that strychnine had been added to a certain breakfast cereal to make it more appetizing. The report was false and not even new, for in 1852 it was alleged that strychnine was being added to certain English pale ales. In order to show that strychnine could be detected in beer if present, Graham and Hofmann[2] shook two ounces of animal charcoal with half a gallon of beer to which 1/2 grain of strychnine had been added. The strychnine was removed practically completely by the charcoal, and was extracted from that with alcohol and identified.

[1] Lake: Jour. Phys. Chem., **20**, 761 (1916).

[2] Jour. Chem. Soc., **5**, 713 (1853).

Skey[1] reports that dilute sulphuric acid can be freed from traces of nitric acid by shaking with charcoal, while concentrated sulphuric acid cannot be. Dudley[2] showed that the rank and disagreeable odor of raw whiskey can be removed by leaching through charcoal. Schmidt[3] has studied the simultaneous adsorption of iodine and acetic acid by charcoal from solution in water and in ethyl acetate. With both solvents less of each substance was adsorbed than if the other had not been present. Schmidt believes that this is general, but this statement is undoubtedly too broad, though it holds in many cases. Freundlich and Masius[4] studied the adsorption of pairs of organic acids and obtained results similar to those of Schmidt. They also found that the acid, which is adsorbed more, is displaced less when the two acids are present in the solution. These experiments throw light on Skey's experiments. With increasing relative concentration of sulphuric acid, we should expect an increasing displacement of nitric acid from the charcoal, which is what actually occurred. Lachs and Michaelis[5] found that caustic potash cut down very much the adsorption of potassium chloride by charcoal from water. In other words, the presence of the strongly adsorbed hydroxyl ion decreased the adsorption of the chloride very much. They also found that if sulphuric acid is added in small amounts to the chloride solution the adsorption of chloride ion is increased markedly. This is in accord with the results of Osaka,[6] that potassium chloride is adsorbed more than potassium sulphate, or sodium sulphate, and, presumably, hydrochloric acid more than sulphuric acid.

Thorium salts cut down the adsorption of uranium X by charcoal[7] and acetone and acetic acid decrease the adsorption of grape-sugar by charcoal[8] but albumin and acetone have no effect

[1] Chem. News, **17,** 217 (1886).
[2] Jour. Am. Chem. Soc., **30,** 1784 (1908).
[3] Zeit. phys. Chem., **74,** 730 (1910).
[4] Van Bemmelen Gedenkboek, 88 (1910).
[5] Zeit. Elektrochemie, **17,** 1 (1911).
[6] Mem. Coll. Sci. Kyoto Univ., **1,** 267 (1915).
[7] Freundlich and Kaempfer: Zeit. phys. Chem., **90,** 681 (1915).
[8] Rona and Michaelis: Biochem. Zeit., **16,** 499 (1909).

on each other, nor does one acid dye apparently displace another on wool or silk.[1]

If we have two salts with no common ion, it is easy to see that the most strongly adsorbed cation and anion will be taken up the most, while the other pair will be adsorbed the least readily. In the case of dyeing we have an admirable illustration of the fact, first recognized by Lachs and Michaelis,[2] and by Estrup,[3] that an anion is adsorbed more readily in presence of a readily adsorbed cation and a cation in presence of a readily adsorbed anion. In an acid dye the color is in the acid radical and in a basic dye the color is in the basic radical. An acid dye will therefore be taken up more strongly in an acid solution than in a neutral solution and will be taken up least in an alkaline solution. A readily adsorbed anion will decrease the amount of dye taken up and a readily adsorbed cation will increase it. With a basic dye the reverse will be true. The dye will be taken up most readily in an alkaline solution but may be taken up in a natural or acid solution. A readily adsorbed cation will cut down the adsorption of the dye and a readily adsorbed anion will increase it.

In Tables XXXI–XXXII are data by Pelet-Jolivet[4] for crystal ponceau, an acid dye.

TABLE XXXI.—ADSORPTION OF CRYSTAL PONCEAU BY WOOL

Volume of solution = 200 cc.
Weight of wool = 5 grams.
x = percent crystal ponceau.

x	Milligrams crystal ponceau adsorbed		
	3 cc N/10 H_2SO_4	Water	0.12 g Na_2SO_4
0.1	65	41.7	36.2
0.2	113	62.8	59.8
0.3	150	76.5	64.8
0.4	178	86.5	70.8

[1] LAKE: Jour. Phys. Chem., **20,** 751 (1916).
[2] Zeit. Elektrochemie, **17,** 1 (1911).
[3] Zeit. Kolloidchemie, **11,** 8 (1912).
[4] Die Theorie des Färbeprozesses, 94, 149 (1910).

TABLE XXXII.—ADSORPTION OF CRYSTAL PONCEAU BY WOOL

Volume of solution = 200 cc.
Weight of wool = 5 grams.
Crystal ponceau = 0.372 mg.

cc N/10 acid added	Milligrams crystal ponceau adsorbed		
	HCl	H_2SO_4	H_3PO_4
0	44	42	42
8	109	93	48
18	158	140	80
28	171	153	102

In acid solution crystal ponceau is adsorbed more strongly than in a water solution, while the presence of the strongly adsorbed anion of sodium sulphate cuts down the adsorption over that in water. In the acid solution the strongly adsorbed phosphate anion works against the strongly adsorbed hydrogen cation and consequently the dye is least adsorbed in a phosphoric acid solution and most adsorbed in a hydrochloric acid solution.

In Tables XXXIII and XXXIV are data by Pelet-Jolivet[1]

TABLE XXXIII.—ADSORPTION OF METHYLENE BLUE BY SILK AND COTTON

A = 0.3 gram silk in 50 cc 0.2 percent methylene blue.
B = 3 grams cotton in 100 cc 0.1 percent methylene blue.

Fiber	Methylene blue adsorbed, mg		
	2 cc N/10 HCl	Neutral solution	2 cc N/10 KOH
Silk (A)	1.3	10.8	40.6
Cotton (B)	1.2	11.2	30.0

for methylene blue, a basic dye. The most dye is taken up in the alkaline solution and the least in the acid solution which is just as it should be. For the same concentration of acid, more dye is taken up in a phosphate solution than in a sulphate solution while still less is adsorbed from a hydrochloric acid solution; and we should expect the phosphate radical to be adsorbed the

[1]DieTheorie des Färbeprozesses, 95 (1910).

most and the chlorine radical the least. This comparison is not strictly accurate because equivalent concentrations of two acids do not necessarily mean equal degrees of acidity. On the other hand the amount of hydrogen as ion in 20 cc N/10 H_2SO_4

TABLE XXXIV.—ADSORPTION OF METHYLENE BLUE BY WOOL

Volume of solution = 200 cc.
Weight of wool = 3 grams.
Concentration of methylene blue = 0.8 percent.

Acid added	Methylene blue adsorbed, mg		
	N/10 HCl	N/10 H_2SO_4	N/10 H_3PO_4
0	156	156	152
10	22	37	79
20	20	27	32
30	17		

is unquestionably greater than in 10 cc N/10 HCl after both have been diluted to 200 cc, and, yet, more methylene blue is taken up in this sulphuric acid solution than in the hydrochloric acid solution. The difficulty in regard to the acidity can be got round by adding salts. Some data[1] are given in Table XXXV. At

TABLE XXXV.—ADSORPTION OF METHYLENE BLUE BY WOOL

Volume of solution = 100 cc.
Weight of wool = 1 gram.

Methylene blue in solution, percent	Methylene blue adsorbed, mg		
	No salt	0.06 g Na^2SO_4	0.06 g Na_2HPO_4
0.1	35	45.6	81.1
0.2	40	52.2	91.3
0.3	43	56.4	95.6
0.4	44	59.4	98.6

every concentration of dye more dye is fixed in the bath containing sulphate than in the bath to which no salt is added, while still more dye is adsorbed in the phosphate solution. We see

[1] Pelet-Jolivet: Die Theorie des Färbeprozesses, 118 (1910).

thus the amount of adsorption varying in the order $Na_2HPO_4 > Na_2SO_4 > NaCl > H_2O$. Just as should be the case, sodium sulphate increases the amount of a basic dye taken up, whereas it decreases the amount of an acid dye adsorbed. With 0.5 gram silk in 50 cc 0.2 percent methylene blue solution, the amounts of methylene blue taken up were 28.6, 18.4, 13.3, and 10.8 mg when sodium phosphate, sodium sulphate, sodium chloride, and nothing were added respectively to the solution.[1] With cotton there was no difference under the same circumstances; but there was a marked difference when the cotton had been treated with tannin. The effect of different cations was also studied by Pelet-Jolivet who found that silk took up 13.3 mg methylene blue from a solution containing sodium chloride and only 6.3 mg from a solution containing barium chloride, the strongly adsorbed barium cation thus cutting down the adsorption of the basic dye. With wool the depth of color decreases in the following order: sodium phosphate, sodium sulphate, no addition, barium chloride, and platinum tetrachloride. Cotton takes up less methylene blue from a solution containing barium chloride than from one containing sodium chloride.

With substantive dyes the effects of electrolytes are different because these dyes are in colloidal solution and the question of stability enters in. Abnormal results are also to be expected with acid and basic dyes which form colloidal solutions.

When an acid dye is adsorbed nearly completely by the fiber it may easily happen that the differences between acids becomes so small as to be practically negligible.[2] The concentration of the anion can be increased very much relatively to the concentration of hydrogen as ion by adding salt, and thus the effect of the anion can be brought out. This is shown in Table XXXVI. In the third column are given the amounts of dye adsorbed when acids alone are added to the bath. In the fifth column are the amounts of dye adsorbed when the solution contains 10 cc N/10 acid + 10 cc N/1 salt. With the acids alone the amount of adsorption of acid violet is practically independent of the nature of the acid. With croceine orange, sulphuric acid and phosphoric acid behave practically alike and cut down the adsorption as compared with

[1] Pelet-Jolivet: Die Theorie des Färbeprozesses, 118 (1910).

[2] Lake: Jour. Phys. Chem., **20**, 785 (1916).

hydrochloric acid. With acid violet the addition of sodium chloride has no appreciable effect. The slight apparent increase in adsorption is probably due to experimental error. With croceine orange the sodium chloride cuts down the adsorption slightly. With sodium phosphate the effect is quite extraordinary,

TABLE XXXVI.—ADSORPTION OF ACID VIOLET AND CROCEINE ORANGE BY WOOL

Volume of solution = 250 cc.
Weight of wool = 1 gm.
Amount of dye = 40 mg.
Temperature = 100°.
Time of run = 1 hr.

Acid dye	10 cc N/10 acid	Adsorbed dye, mg	Acid + 10 cc N/1 salt	Adsorbed dye, mg
Acid violet.....	HCl	39.2	NaCl	39.5
	H_2SO_4	39.2	Na_2SO_4	36.8
	H_3PO_4	39.1	Na_2HPO_4	1.0[1]
Croceine orange.....	HCl	38.0	NaCl	33.4
	H_2SO_4	35.5	Na_2SO_4	20.0
	H_3PO_4	35.5	Na_2HPO_4	0.1[1]

the adsorption of acid violet and of croceine orange being cut almost to zero. The change in the hydrogen ion concentration cannot account for this because 38 mg acid violet and 32 mg croceine orange are adsorbed from a water solution under similar circumstances. We are therefore dealing with a specific effect of the phosphate radical.

Qualitative experiments along the same lines have been obtained by Davison.[2] With acid green and emerald green on wool and with fast green and safranine on cotton, good illustrations are obtained of the generalization that acid dyes are taken up more completely in an acid solution than in a neutral one and least of all in an alkaline solution, while the reverse is true with basic dyes. Marked differences between the dyeing in acid and alkaline solutions can be obtained on wool with fast green, fast blue, acid violet, croceine orange, crystal ponceau, chrysoidine, safranine, and methylene blue; on cotton with

[1] These experiments are probably not strictly comparable with the others owing to the change in hydrogen ion concentration.

[2] Jour. Phys. Chem., **17**, 737 (1913).

acid violet, croceine orange, and emerald green. The generalization that addition of sodium sulphate cuts down the adsorption of acid dyes and increases the adsorption of basic dyes is shown excellently on wool with acid green, fast blue, croceine orange, Victoria blue, chrysoidine, and safranine; on cotton with benzopurpurine. The effect of continuously varying concentrations of sodium sulphate is shown well on wool with brilliant blue and safranine; on cotton with safranine. When alumina is precipitated from an aluminum acetate solution, it adsorbs fast green, acid green, and croceine orange considerably; but when precipitated from an aluminum sulphate solution it carries down practically no fast green, acid green, or croceine orange. The presence of sulphate decreases the adsorption of acid dyes by alumina as well as by wool. Another illustration of this is that alumina precipitated from an aluminum sulphate solution can only decolorize dilute solutions of alizarine, alizarine green, benzo orange, coeruleine, and acid violet, while alumina precipitated from an acetate solution will decolorize more concentrated solutions. In these experiments with alumina the dye was added to the solution before the alumina was precipitated. It seems probable that if alumina were precipitated from a sulphate solution with barium hydroxide or calcium hydroxide, the effect due to the sulphate would disappear owing to the insolubility of the barium or calcium sulphate. This experiment was not tried.

Chemical Action

Selective adsorption connotes the possibility of chemical decomposition as a result of adsorption. If a given substance adsorbs a base more strongly than an acid for instance, there will be a tendency for the salt of that base and that acid to hydrolyze, the base being then adsorbed to a greater extent than the acid. Theoretically there is always some hydrolysis even with sodium chloride and water according to the equation

$$Na^{\cdot} + Cl' + H_2O = Na^{\cdot} + OH' + H^{\cdot} + Cl'$$

but this reaction does not run far because caustic soda and hydrochloric acid are strong electrolytes and we cannot have a high simultaneous concentration of hydrogen and hydroxyl as ions. If the caustic soda is removed by adsorption, the hydrolysis can go farther. How complete the hydrolysis will be

depends on the degree to which the base is adsorbed and on the strength of the acid. Any acid will tend to react with adsorbed caustic soda; but that tendency will be greater the stronger the acid. We thus see that a neutral solution will become acid if shaken with a substance which adsorbs the base much more strongly than the acid, that it will become alkaline if the substance adsorbs the acid much more strongly than the base, and that it will remain neutral in case the solid does not adsorb either base or acid at all, or in case it adsorbs the two in practically equivalent amounts either separately or as undissociated salt. The amount of base or of acid taken up from a salt solution will be greater the weaker the unadsorbed acid or base. Many cases are known where the solution does become acid or alkaline when shaken with an adsorbing agent and this has nothing to do with any hypothetical acidity or alkalinity of the adsorbing substance.

If fuller's earth be shaken with water and then filtered, the filtrate is neutral to litmus paper[1] or to phenolphthalein, showing that no soluble base or acid is present. If fuller's earth be shaken with a sodium chloride solution and filtered, the filtrate is acid to litmus or to phenolphthalein. This is because fuller's earth has adsorbed the base. If one presses litmus paper against moistened fuller's earth, the litmus paper turns red, and if one adds fuller's earth to a faintly alkaline solution of phenolphthalein, the red color disappears. This is not because the fuller's earth is acid, but because it takes the base from the sodium chloride, the litmus, or the phenolphthalein.

I have been told that the adsorbing power of fuller's earth is so great that an acre-foot as soil would adsorb 30,000 lb. of lime and that this would make fuller's earth about equivalent in acidity to a two percent sulphuric acid solution.

Silk has such a marked selective adsorption for rosaniline (magenta) that it will not only decompose the hydrochloride, leaving the acid behind, but will also convert the carbinol base back into the color base in presence of an excess of ammonia,[2] the silk being dyed red from a colorless ammoniacal solution.

[1] Cf. CAMERON: Jour. Phys. Chem., **14,** 400 (1910).

[2] JACQUEMIN: Comptes rendus, **82,** 261 (1876); see also MILLS: Jour. Chem. Soc., **35,** 27 (1879); FORTUYN: Zeit. phys. Chem., **90,** 236 (1915.)

This is the more remarkable because the free color base is instable and cannot be isolated in a pure state. This makes it seem certain that silk stabilizes the free color base. Another similar instance is the mordanting of wool with copper salts, coloring it green. This green does not change to black when the wool is heated to boiling, though hydrous copper oxide by itself changes very readily. Blucher and Farnau[1] have extended Tommasi's[2] experiments on the stabilization of hydrous copper oxide by manganese salts and find that a number of other metallic hydroxides are also effective. Bayliss[3] has obtained results, which indicate that alumina stabilizes the free acid of Congo red, and Schaposchnikoff and Bogojawlenski[4] have isolated this metastable form by allowing the pyridine salt to effloresce. Passive iron is an instable oxide, presumably FeO_2 or FeO_3, stabilized when adsorbed by metallic iron.[5]

When discussing the adsorption of gases by solids, numerous instances were given of so-called contact catalysis. With solutions the effect of contact materials is as yet relatively unimportant. Lassar-Cohn[6] gives a few instances where yields have been increased by the use of porous masses. When two parts of acetanilide were heated with one part of zinc chloride, a yield of 3.5 percent flavaniline hydrochloride was obtained. In presence of two parts of infusorial earth the yield increased to about 7.5 percent. When benzene and chloroform react in presence of aluminum bromide, the yield increases from 33 percent to 44 percent when infusorial earth is added. The sulphonation of benzene, xylene, naphthalene, anthraquinone, aniline, etc., is simplified very much by the addition of infusorial earth or of charcoal. When α-dinitronaphthalene is treated with sulphuric acid under suitable conditions in presence of infusorial earth or charcoal, oxidation takes place with elimination of the nitro groups and formation of naphthazarin.

[1] Jour. Phys. Chem., **18,** 629 (1914).

[2] Tommasi: Bull. Soc. chim. Paris (2) **37,** 197 (1882); Comptes rendus **99,** 37 (1884).

[3] Proc. Roy. Soc., **84B,** 881 (1911).

[4] Jour. Russ. Phys. Chem. Soc. **44,** 1813 (1913).

[5] Bennett and Burnham: Jour. Phys. Chem., **21,** 107 (1917).

[6] Arbeitsmethoden für organisch-chemische Laboratorien, 584, 72, 1079, 923 (1903).

Gurwitsch[1] reports that amylene polymerizes readily on standing in contact with "floridin," which is a hydrous silicate of some sort. Playfair[2] found that a solution of nitric acid could be prepared which would only bleach a piece of cloth dyed with indigo when the cloth was in contact with alumina, chromic oxide, or stannic oxide. Richardson[3] believes that petroleum and bitumens are formed by the polymerizing or condensing action of clays or sands.

A case which has been studied a great deal quantitatively is the decomposition of hydrogen peroxide solutions by platinum. One of the most interesting things about this reaction is its extreme sensitiveness to so-called poisons.[4] The rate of decomposition of hydrogen peroxide by a given solution of colloidal platinum was reduced approximately to one-half by M/20,000,000 HCN, M/2,000,000 $HgCl_2$, and M/300,000 H_2S. Curiously enough the catalytic action of platinum and of ferments on hydrogen peroxide is decreased in both cases by very slight traces of poisons, such as prussic acid, hydrogen sulphide, etc. It has also been shown by Schönbein[5] that these same substances cut down the catalytic action of red blood corpuscles on hydrogen peroxide.

In Table XXXVII are given data[6] for the concentrations necessary to cut down the rate of decomposition of hydrogen peroxide to one-half in the case of colloidal platinum and of haemase, the active enzyme in the red blood corpuscles. While many of the substances that cut down the platinum catalysis also decrease the catalytic action of haemase, there are many cases where no parallelism occurs. Thus carbon monoxide is very toxic to platinum and has no effect on haemase. On the other hand, nitric acid, sulphuric acid, potassium nitrate, and potassium chlorate have practically no effect on platinum and are quite toxic to haemase. Even where there is a general parallelism, one must not follow it too closely. With platinum the prussic acid solution

[1] Zeit. Kolloidchemie, **11,** 18 (1912).

[2] Mem. Chem., Soc. **3,** 354 (1847).

[3] Jour. Ind. Eng. Chem., **8,** 4 (1916); Met. Chem. Eng., **16,** 25 (1917).

[4] Bredig and von Berneck: Zeit. phys. Chem., **31,** 258 (1899); Bredig and Ikeda: Ibid., **37,** 1 (1901).

[5] Jour. prakt. Chem., **105,** 202 (1868).

[6] Senter: Zeit. phys. Chem., **51,** 701 (1905).

has one-tenth the concentration of the mercuric chloride solution, while with haemase it has double the concentration. The tabulated concentration for mercuric chloride is the same for platinum as for haemase, while that of iodine dissolved in potassium iodide is one hundred times as great for haemase. Kastle and Loevenhart[1] point out that prussic acid is a strong poison for colloidal

TABLE XXXVII.—THE POISONING OF COLLOIDAL PLATINUM AND HAEMASE

Concentrations at which poisons reduce the rate of the catalytic decomposition of hydrogen peroxide approximately to one-half.

Poison	Colloidal platinum	Haemase
H_2S	M/300,000	M/1,000,000
HCN	M/20,000,000	M/1,000,000
$HgCl_2$	M/2,000,000	M/2,000,000
$HgBr_2$		M/300,000
$Hg(CN)_2$	M/200,000	M/300,000
I_2 in KI	M/5,000,000	M/50,000
$NH_2OH.HCl$	M/25,000	M/80,000
Phenyl hydrazine		M/20,000
Aniline	M/5,000	M/400
Arsenious acid	M/50	No poisoning at M/2,000
CO	Very poisonous	No poisoning
HCl	M/3,000	M/100,000
NH_4Cl	M/200	M/1,000
HNO_3	No poisoning	M/250,000
H_2SO_4	No poisoning	M/50,000
KNO_3	No poisoning	M/40,000 at 0°
$KClO_3$	Slight poisoning?	M/40,000 at 0°

platinum and silver but accelerates the catalysis of hydrogen peroxide by iron and copper.

It seems probable that the poisons are adsorbed strongly by the catalytic agent and therefore prevent the adsorption of hydrogen peroxide.[2] This adsorption will be specific and will therefore in general not be the same quantitatively for different catalytic agents. On the other hand, there may well be a qualitative agreement in some or even in many cases. Owing to the extreme

[1] Am. Chem. Jour., **29**, 397 (1903).

[2] Cf. SENTER: Zeit. phys. Chem., **51**, 702 (1905); DENHAM: Ibid., **72**, 689 (1910).

flexibility of this hypothesis there is nothing as yet to prevent its accounting for all the phenomena observed.[1] On the other hand it must be remembered that proof is still lacking that platinum adsorbs prussic acid for instance, very much more strongly than hydrogen sulphide, and that there is no difference with haemase. There may be other factors which must be taken into account. Thus Bredig[2] points out that when colloidal platinum is allowed to stand in contact with hydrogen peroxide and concentrated potassium cyanide, the platinum flocculates and precipitates. The agglomerated platinum causes the hydrogen peroxide to decompose, thus showing that the cyanide does not poison precipitated platinum black. There seem to be only two possible explanations. One is that the adsorption of potassium cyanide by platinum falls off very much more rapidly with increasing size of the platinum particles than the adsorption of hydrogen peroxide by platinum. The other explanation is that, through oxidation or otherwise, there is formed what might be called an anti-body, which cuts down the adsorption of the cyanide. Neither hypothesis is very satisfactory and there is no experimental evidence for either, except that Jablczynski[3] found that platinized platinum decomposes chromous chloride three times as fast and hydrogen peroxide one hundred times as fast as does smooth platinum foil. The matter should be taken up because Rosnyak[4] claims that the catalytic action of platinum on hydrogen peroxide decreases with increasing dispersity of the platinum and Felgate[5] states that pulverulent nickel reduces nitric oxide while colloidal nickel does not. In both these cases it is probable that some factor has been overlooked or not stated. The more finely divided the platinum the more likely the surface is to be coated with oxide and it does not follow at all that the catalytic action of metallic platinum is the same as that of an oxide of platinum. If platinum is kept in suspension by means of gelatine or some similar substances, this will have an effect on the adsorption and the catalytic action.

[1] Cf. Freundlich and Kaempfer: Zeit. phys. Chem., **90,** 681 (1915).
[2] Zeit. phys. Chem., **31,** 332 (1899).
[3] Ibid. **64,** 751 (1908).
[4] Ibid. **85,** 68 (1913).
[5] Chem. News, **108,** 178 (1913).

A comparatively recent technical development in contact catalysis is the hardening of oils, by the conversion of oleic acid or olein, for instance, into stearic acid or stearin by the action of hydrogen on the liquid unsaturated oil in presence of a suitable catalytic agent.[1] In 1908 Paal[2] proposed using a colloidal metal as the catalytic agent at ordinary temperatures. Colloidal solutions of platinum, palladium, osmium, and iridium have been made, of which the palladium hydrosol appears to possess the greatest value. When hydrogen at ordinary temperatures is passed into glycerides of the unsaturated fatty acid to which some palladium hydrosol has been added, reduction takes place. It is more satisfactory, however, to precipitate the metal on an inert base such as magnesia or kieselguhr.

A cheaper and apparently better method is to use nickel as a catalytic agent for the hydrogenation of liquid, unsaturated acids, the reduction taking place at about 250°–300°. There has been some controversy whether the catalytic agent was really metallic nickel[3] or an unspecified oxide or oxyhydride;[4] but there seems to be little doubt but that the metal is the catalytic agent. Some details in regard to the preparation of the catalytic agent are given by Ellis.[5] Paal and Karl[6] report that the oxides of lead, cadmium, zinc, aluminum and iron cut down the catalytic action of palladium, while the oxides of magnesium, nickel, and cobalt do not.

Adsorption from Solution by Liquid

There is no reason why there should not be adsorption by a liquid just as well as by a solid, except that the matter is complicated by the possibility of the solute dissolving in the second

[1] Jobling: Catalysis and its Industrial Applications, 65, 75 (1916).

[2] Ber. deutsch. chem. Ges., **41,** 2282 (1908).

[3] Meigen: Jour. prakt. Chem. (2) **92,** 390 (1915).

[4] Bedford and Erdmann: Jour. prakt. Chem. (2) **87,** 425 (1913); Siegmund and Saida: Ibid. (2) **91,** 442 (1915); Erdmann: Ibid. (2) **91,** 469 (1915); Glaser: Zeit. anorg. Chem., **36,** 1(1903); Bellacci and Corelli: Ibid., **86,** 88 (1914); Sabatier and Espil: Comptes rendus, **158,** 568; **159,** 137 (1914).

[5] Jour. Soc. Chem. Ind., **31,** 1163 (1912); The Hydrogenation of Oils, 2d. Ed., 108 (1918).

[6] Ber. deutsch. chem. Ges., **46,** 3069 (1913).

liquid. An interesting case of such adsorption was studied by Wilson,[1] Swan,[2] and Twomey.[3] When a drop of chloroform or carbon tetrachloride is placed on the bottom of a glass dish and water or dilute acid poured over it, the drop is well rounded. If the solution is made alkaline, the drop flattens out. The flattening is clearly not due to a change in surface tension of the water phase, because Wilson found that the effect of alkali was the same qualitatively whether sodium chloride was present or not, whereas the addition of salt increases the surface tension of the water phase. What happens is that hydroxyl is adsorbed at the dineric interface, lowering the surface tension and causing the organic liquid to flatten. This is confirmed by the experiments of von Lerch[4] who determined the surface tension between benzene and water by means of the rise in capillary tubes.[5] The surface tension between pure benzene and pure water was found to be 32.6 dynes/cm at 15°–16°. With M/4 NaOH the value dropped to 20.7 and with M/2 NH_4OH to 27.3. The lowering of the surface tension is greater with sodium hydroxide than with ammonia owing to the greater electrolytic dissociation of the former. The surface tension was also lowered by hydrochloric acid but only slightly, M/2 HCl bringing it down to 31.5. This is in accord with Wilson's qualitative conclusions that acids do not increase the surface tension quite as much as pure water. Von Lerch also found a marked effect due to acetic acid; but this acid is miscible in all proportions with benzene and causes benzene and water to become more miscible, so there is nothing surprising about its behavior. The surface tension measurements are confirmed by the electrical ones, for von Lerch found that drops of benzene in caustic soda moved fairly readily under electrical stress, whereas there was almost no movement in presence of sodium chloride or hydrochloric acid. It is possible that other ions might be adsorbed markedly by benzene, but I know of no experiments to show this. Patrick[6] found that new fuchsine,

[1] Jour. Chem. Soc., **1,** 174 (1849).

[2] Phil. Mag. (3) **33,** 36 (1848).

[3] Jour. Phys. Chem. **19,** 360 (1915).

[4] Drude's Ann., **9,** 434 (1902).

[5] Harkins states that von Lerch's experiments with dilute caustic soda solution are inaccurate.

[6] Zeit. phys. Chem., **86,** 545 (1914).

picric acid, salicylic acid, and mercurous sulphate are adsorbed from aqueous solution by mercury, the surface tension of the mercury being lowered as a result of the adsorption. In all four cases the amounts adsorbed varied with the concentration approximately according to a formula of the type found to hold for adsorption from solution by a solid.

The adsorption of hydroxyl means practically a concentrating of alkali at the surface of the benzene and consequently a closely adhering film of water. This accounts for Wilson's observation that the drops of chloroform were readily wetted by an alkaline solution. The presence of the surface film of caustic soda solution also accounts for the decreased mobility observed by Wilson.

CHAPTER IV

SURFACE TENSION—BROWNIAN MOVEMENTS

Adsorption and Surface Tension

When a substance dissolves in a liquid, the surface tension between the liquid and the vapor changes, increasing in some cases and decreasing in others. Two solutions of the same density will not necessarily have the same surface tension. For this reason a hydrometer graduated for sulphuric acid solutions will not be accurate for hydrochloric acid solutions, because the amounts of solution which will rise up the stem of the hydrometer will depend on the surface tensions and will therefore not be the same in the two cases. In most cases the surface tensions of solutions will lie between the surface tensions of the constituents; but this is not necessarily true.[1] Röntgen and Schneider[2] found a maximum surface tension for sulphuric acid and water at about 48 percent H_2SO_4. Whatmough[3] obtained minima for mixtures of acetic acid with benzene, methyl iodide, ethyl iodide, chloroform, or carbon tetrachloride; for carbon bisulphide and ethylene chloride; for benzene and ethyl iodide; for carbon tetrachloride and chloroform, for ethyl acetate and amyl alcohol. Most salts increase the surface tension of the solution, the increase being very nearly proportional to the concentration. The strong bases increase the surface tension but ammonia lowers it and so also do nitric, hydrochloric, and hydrobromic acid. Worley[4] has discovered an interesting fact. Although sodium chloride increases the surface tension of water, the addition of salt to a solution of aniline in water decreases the surface tension. The sodium chloride decreases the solubility of aniline in water and therefore increases the partial pressure of the aniline vapor.

[1] See Freundlich: Kapillarchemie, 58 (1909).
[2] Wied. Ann., **29,** 165 (1886).
[3] Zeit. phys. Chem., 39, 129 (1902).
[4] Jour. Chem. Soc., **105,** 260, 273 (1914).

The vapor pressures therefore correspond to a solution richer in aniline than that actually present and the surface tension relations run approximately parallel with the vapor pressures. Worley noticed another curious thing in regard to change of surface tensions of solutions with rising temperature. Since liquid and vapor are identical at the critical temperature, the surface tension becomes zero at the critical point and the surface tension of pure liquids therefore decreases with rising temperature. One might reasonably have expected that the surface tension temperature curves for solutions would run somewhere near parallel to the corresponding curves for the pure constituents; but this is not the case for mixtures of water with aniline or phenol. The surface tension of the phenol-rich solutions vary relatively little with rising temperature, while the corresponding aniline solutions actually show an increase of surface tension with rising temperature, The explanation seems to be that the ratio of water to aniline or phenol in the vapor increases with rising temperature and that the solutions therefore show surface tensions corresponding to what one might expect of solutions richer in water than they actually are. It is a pity that Worley did not also study some such case as ether and water, where the partially miscible liquid with the lower surface tension has the higher vapor pressure.

The change in surface tension when a solution is formed is also accompanied by a change in concentration, the surface film of the liquid having a different concentration from the mass of the liquid solution. The simple rule in regard to this is that the concentration in the film tends to change so as to decrease the surface tension.[1] Consequently the surface film will be more dilute than the mass of the solution if the dissolved substance increases the surface tension, and will be more concentrated than it, if the solute lowers the surface tension of the solution. An equilibrium will be reached when the change in the surface tension is balanced by the difference of osmotic pressure between the surface film and the mass of the solution. This can be expressed mathematically by the equation[2]

$$\gamma = -\frac{da}{d\mu}$$

[1] J. Willard Gibbs: Scientific Papers, **1**, 219.

[2] Cf. Donnan and Barker: Proc. Roy. Soc., **85A**, 557 (1911).

where a is the interfacial tension, μ is the chemical potential of the dissolved substance in the aqueous phase, γ is the mass of solute per unit area of interface in *excess* of that corresponding to the uniform bulk-concentration of the solute in the solution. It will be seen that γ is, in fact, the amount of solute per unit area of interface adsorbed or concentrated in the interfacial transition layer. If we are justified in applying the laws of dilute solutions, the above equation can be written

$$\gamma = -\frac{c}{RT}\frac{da}{dc}$$

where R is the constant of the simple gas equation, T is the absolute thermodynamic temperature and c is the concentration. It is to be noted that these two equations apply only to the case of a substance which is really in solution, a point which is apt to be overlooked in papers on colloids. On the other hand, there are many substances such as soap, saponin, gelatine, which are probably not soluble in water to any appreciable extent; but which form apparent or colloidal solutions with surface tensions lower than those of pure water. In these cases the concentration of the added substance will be higher in the surface film than in the mass of the liquid, but the Gibbs formula will not apply. As a matter of fact with sodium glycocollate, Congo red, methyl orange, and sodium oleate, the adsorptions in the surface are 20–100 times those calculated from the formula.[1]

If the difference in concentration between the mass of the solution and the surface layer is set up slowly, one ought to get one value for the surface tension when equilibrium is reached and another if rapid measurements are made on a fresh surface. This has been done by Lord Rayleigh,[2] though not for a case of true solution.[3] The equilibrium or static method consisted in measuring the rise in capillary tubes. The rapid or dynamic method depends on the principle that a jet of liquid issuing under moderate pressure from an elongated, *e.g.*, elliptical, aperture

[1] Willows and Hatschek: Surface Tension and Surface Energy, 46 (1915).

[2] Proc. Roy. Soc., **47**, 281 (1890).

[3] See however Harkins and Brown: Jour. Am. Chem. Soc., **41**, 522 (1919).

perforated in a thin plate, assumes a chain-like appearance, the complete period, λ, corresponding to two links of the chain, being the distance traveled over by a given part of the liquid in the time occupied by a complete transverse vibration of the column about its cylindrical configuration of equilibrium. Since the phase of vibration depends upon the time elapsed, it is always the same at the same point in space, and thus the motion is *steady* in the hydrodynamical sense, and the boundary of the jet is a fixed surface. Measurements of λ under a given head, or velocity, determine the time of vibration, and from this, when the density of the liquid and the diameter of the column are known, follows in its turn the value of the capillary tension to which the vibrations are due. By this method the liquid surface may be tested before it is $\frac{1}{1000}$ second old.

Rayleigh's data have been recalculated by Freundlich[1] who added some of his own. These are given in Table XXXVIII.

TABLE XXXVIII.—STATIC AND DYNAMIC SURFACE TENSIONS OF SOLUTIONS

Solution	Concentration	Surface tensions in dynes/cm	
		Static	Dynamic
Water		75	75
Sodium oleate	0.025 percent	55	79
Sodium oleate	0.25 percent	26	79
Sodium oleate	1.25 percent	26	62
Sodium oleate	2.5 percent	26	58
Saponin		52	73
Heptylic acid	0.005*N*	54	68

Except in the case of pure water the surface tensions by the static method are lower than those by the dynamic method. One curious point is that the surface tensions by the dynamic method are higher than that of pure water in the case of the two very dilute sodium oleate solutions. Lord Rayleigh did not discuss this point and Freundlich leaves it untouched. In the actual measurements an error of about two percent would account for the difference, which may be due to experimental error. There is another possibility, however, that the sodium oleate is completely

[1] Kapillarchemie, 56 (1909).

hydrolyzed in the dilute solutions and that what is measured by the dynamic method is really the surface tension of a caustic soda solution.

While this set of experiments gives more or less the results that one would expect, it seems impossible to account for the difference between the static and dynamic methods in the case of the adsorption of gases by mercury. Stöckle[1] measured the surface tension of mercury in a vacuum of 0.004–0.001 mm and obtained a value of 436 dynes/cm at 15° regardless whether the measurement was made at once or not. When hydrogen was present, the time factor was important, a value of 470 dynes/cm being obtained when the measurement was made quickly, but dropping to 434 dynes/cm if the mercury were allowed to stand in contact with hydrogen. Similar results were obtained with oxygen, nitrogen, carbon dioxide, and air, Table XXXIX. The general results were confirmed by G. Meyer,[2] Table XL, who made

TABLE XXXIX.—SURFACE TENSION OF MERCURY

Data in dynes/cm with fresh and old surfaces

Medium	Rapid	After 60′
Vacuum (15°)	436	434
Hydrogen (21°)	470	436
Oxygen (25°)	478	432
Nitrogen (16°)	489	438
Carbon dioxide (19°)	...	429
Dry air (17°)	476	429
Moist air (17°)	481	

TABLE XL.—SURFACE TENSION OF MERCURY

Data in dynes/cm with fresh and old surfaces

Medium	Vibrating jet	Curvature of surface
Hydrogen	554	470
Oxygen	504	478
Carbon dioxide	487	480
Nitrogen	496	489

[1] Wied. Ann., **66,** 49 (1898).

[2] Ibid., **66,** 523 (1898).

use of Rayleigh's jet method for the rapid measurements and consequently obtained higher values than Stöckle.

It may be easy to see that the adsorption of a gas by mercury should lower the surface tension, but it is not clear why different gases should bring the surface tension down practically to the same value as that found when there is supposed to be no gas present. The dynamic methods should start at the value for mercury in a vacuum if no factor has been overlooked and there is no apparent reason why an unadsorbed gas should raise the surface tension of mercury so much.

Lenard[1] has brought up a point which may have a bearing on this. If we have a partially polymerized liquid such as water, the modification having the lower surface tension will concentrate in the surface. If we form a new surface suddenly, we shall get a higher concentration, temporarily, of the particular modification which has the higher surface tension. If the equilibrium is reached relatively slowly, the dynamic method will give a higher value for the surface tension than the static methods. If equilibrium is reached instantaneously, there will be no difference. We can account for the facts observed with mercury if we make the assumptions that mercury is a partially polymerized liquid, that equilibrium between the modifications is reached practically instantaneously in a vacuum, and that equilibrium is reached relatively slowly in presence of gases. The difficulty with this is that we have no independent proof of these assumptions.

Another hypothetical explanation becomes possible, if we assume that there is not a sharp discontinuity at the surface between liquid and vapor. The Laplace theory of surface tension assumes that there is a perfectly sharp line of demarcation between the two media bounding the surface, for instance,[2] between liquid and air, while van der Waals postulates a continuous transition.

According to the latter way of looking at things, mercury in a vacuum adsorbs its own vapor forming a thin transition layer varying from the density of liquid mercury at one side to the density of mercury vapor at the other side. If this transition

[1] Cf. Aganin: Drude's Ann., **45**, 1020 (1914).

[2] Willows and Hatschek: Surface Tension and Surface Energy, 33 (1915).

film forms instantaneously in a vacuum and relatively slowly in presence of a gas, the surface tension of a fresh surface of mercury in presence of a gas will be higher than the equilibrium surface tension of mercury in a vacuum, and this higher surface tension thus measured will decrease, if the surface is not renewed, down to the equilibrium surface tension of mercury in a vacuum, or below it if the gas is adsorbed markedly at the mercury surface. This explanation seems somewhat more plausible than that of Lenard; but it is open to the same objection that there is as yet no independent proof of the assumptions involved.

Ferguson[1] has shown that the surface tension of benzene is different in air from what it is in carbon dioxide. It is a question of course to what extent this difference is due to the solubilities of the gases in the benzene. Ferguson considers that the nature of the gas is more important than the solubility effect; but he gives no evidence for this. He does, however, mention one interesting and surprising fact that the absolute value of the surface tensions increased slightly as the liquid became more and more saturated, finally reaching a steady value.

From the fact that the lowering of the surface tension is accompanied by an increase in the concentration of the surface film of a true solution, Freundlich[2] draws the conclusion that this is true in all cases, and that if a dissolved substance lowers the surface tension between the solid and the solution, the dissolved substance is adsorbed; conversely that the dissolved substance is adsorbed only in case it lowers the surface tension at the interface. The conclusion may or may not be right; but the logic is faulty because the two cases are not parallel. The Gibbs relation holds for a true solution, where the difference of concentration is entirely inside the solution phase. Freundlich is extending the relation to a heterogeneous system in which the adsorbed substance is presumably on the outer surface of the solid and by definition cannot diffuse into it because we should then have a solid solution. It is very difficult to prove or disprove Freundlich's conclusion experimentally; but it is a great pity to have people believe, as many now do, that the generalization is based on sound thermodynamics.

[1] Phil. Mag. (6) **28**, 403 (1914).

[2] Zeit. phys. Chem., **57**, 424 (1907).

The surface tension of solids cannot be measured directly; but Tangl[1] has made some experiments on the surface tension of such pseudo-solids as rubber and paraffin against water.

Solids undoubtedly do have definite surface tensions. In fact, one might consider the melting point as the temperature at which the surface tension overcomes the crystalline forces. In the liquid crystals and the flowing crystals, we have intermediate stages. Reference has already been made to Beilby's experiments on thin gold leaf which became granular when heated.[2] We shall see later that the phenomenon of sintering depends on surface tension.

Brownian Movements

If a stone be dropped into water, it sinks rapidly; but if it be ground into fine particles, the surface is much greater and consequently the particles sink slowly. If the stone were ground into very fine particles, we should expect these to sink very slowly, the rate being a function of the diameter and density of the particles. A formula,

$$V = \frac{2\,r^2(S - S')g}{9\eta}$$

for this case has been deduced by Stokes,[3] where V is the constant rate of fall, r the radius of the particles, S their specific gravity, S′ the specific gravity of the liquid, η its viscosity coefficient and g the gravitational constant. Hatschek[4] has applied this formula to several special cases. For particles[5] of gold of 1μ radius the rate of fall in water is calculated to be 2.4 mm per minute. With gold particles of $10\mu\mu$ radius the rate of settling in water is about 10 mm per month. For a particle of $10\mu\mu$ radius and a specific gravity of only 3 the calculated rate would be about 1 mm per month. Very small rates of fall have actually been observed.

[1] Drude's Ann., **34,** 311 (1911); cf. Jones: Zeit. phys. Chem., **82,** 448 (1913); Röntgen: Wied. Ann., **3,** 321 (1878).

[2] Proc. Roy. Soc., **72,** 226 (1904).

[3] Mathematical and Physical Papers, **3,** 1 (1901). For modifications and limitations see Cunningham: Proc. Roy. Soc., **83A,** 357 (1910); Jour. Am. Chem. Soc. **41,** 319 (1919); Millikan: Phys. Zeit., **11,** 1097 (1910).

[4] An Introduction to the Physics and Chemistry of Colloids, 24 (1913).

[5] Elutriation, or the difference in the rate of settling, is much used in grading powders such as emery, carborundum, ultramarine, kaolin, etc.

Even in air fine particles settle very slowly. A sandstorm in the Grand Canyon may make the air a brick-red color for two or three days.[1] Similar phenomena are to be observed all over the world.[2]

Ebell[3] states that ultramarine will stay suspended in pure water for months when obtained in a very finely divided state by grinding and elutriation. Mülhauser[4] found that when very finely ground carborundum powder is treated with water, a portion of it does not settle in months and behaves in that respect like colloidal metallic silver. Brewer[5] points out the slow rate at which clays settle, and raises the question whether extremely finely divided particles settle at all.

If the very finely divided particles do not really settle at all, there must be some factor which neutralizes the action of gravity more or less completely. The experiments of an English botanist, Brown,[6] give us a clue to the difficulty, though the importance of these experiments was not appreciated until very much later. Brown was studying under the microscope the grains of pollen from *Clarckia pulchella*, and observed that some of them moved about in the liquid. Further experiments showed that practically all finely divided solids kept in continuous motion. Brown considered that he was watching the movements of active molecules.

The zig-zag movements of suspended particles are known as Brownian movements. They are apparently due to the bombardment of the suspended particles by the molecules of the liquid.[7] On this hypothesis the motion should be more rapid, the smaller the bombarded particles and this proves to be the case. The work of Gouy showed that the hypothesis of molecular agitation gave a satisfactory explanation of the Brownian move-

[1] Ellsworth and Emery Kolb: National Geographical Magazine, **26,** 134 (1914).

[2] See Ehrenberg: Die Bodenkolloide, 209 (1915).

[3] Ber. deutsch. chem. Ges., **16,** 2429 (1883).

[4] Zeit. anorg. Chem., **5,** 117 (1894).

[5] Mem. Nat. Acad. Sci., **2,** 165 (1884); Am. Jour. Sci. (3) **29,** 1 (1885).

[6] Phil. Mag., **4,** 161 (1828); **6,** 161 (1829).

[7] Wiener: Pogg. Ann., **118,** 79 (1863); Gouy: Jour. de Phys. (2) **7,** 561 (1888); Comptes rendus, **109,** 102 (1889); Revue générale des Sciences, **1895,** 1.

ments and that all the other tentative explanations were faulty. He showed that the Brownian movements are not due to vibrations transmitted to the liquid under examination, since they persist equally as well, for example, at night in the country as during the day near a populous street where heavy vehicles pass. They are not due to convection currents existing in fluids where thermal equilibrium has not been attained, for they do not change appreciably when plenty of time is given for equilibrium to be reached. Any comparison between Brownian movements and the agitation of dust particles dancing in the sunlight must therefore be set aside. In addition, in the latter case, it is easy to see that the neighboring dust-particles move in general in the same sense, roughly tracing out the form of the common current which bears them along, whereas the most striking feature of the Brownian movements is the absolute independence of the displacement of neighboring particles, so near together that they pass by one another. The movements cannot be due to an effect of light because Gouy was able to vary the intensity of the illumination abruptly a thousand-fold, or to change the color considerably without modifying the phenomena. The nature of the particles does not appear to be of any importance, and it is therefore difficult not to believe that these particles reveal an internal agitation of the fluid, the better the smaller they are, much as a cork follows better than a large ship the movements of the waves of the sea.

The distance between the two end-points as a particle zigzags forward and back is usually defined as twice the amplitude. Svedberg[1] found that for different solutions the product of the amplitude, A, into the viscosity, η, is a constant and that the amplitude divided by the time which the particles take in passing through that distance is also a constant. These results are in qualitative agreement with a theoretical formula deduced by Einstein.[2] If one knows the amplitude and the time, one can calculate the speed of the particles. For platinum particles with a diameter of 10–50$\mu\mu$, Svedberg found speeds of 200–400$\mu\mu$ per second. Perrin[3] considers that errors of measurements vi-

[1] Zeit. Elektrochemie, **12,** 835, 909 (1906).
[2] Drude's Ann., **17,** 549 (1905); **19,** 289, 371 (1906).
[3] Brownian Movement and Molecular Reality, 22 (1910).

tiate these data. He says that the speed of a granule in suspension cannot be measured accurately.

Even though quantitative measurements may be inaccurate, it is desirable to have a general idea of the magnitude of the phenomenon. From Exner's[1] experiments it appears that particles with a diameter larger than 4μ show no perceptible Brownian movements. Particles smaller than 0.1μ begin to show lively movements,[2] while particles with diameters of about $10\mu\mu$ give apparent trajectories up to $20\mu\mu$.

Perrin[3] came to the conclusion that the gas laws must apply to dilute emulsions. "Let us suppose that it is possible to obtain an emulsion, with the granules all identical, an emulsion which I shall call for shortness, uniform. It appeared to me, at first intuitively, that the granules of such an emulsion should distribute themselves as a function of the height in the same manner as the molecules of a gas under the influence of gravity. Just as the air is more dense at sea-level than on a mountain-top, so the granules of an emulsion, whatever may be their initial distribution, will attain a permanent state where the concentration will go on diminishing as a function of the height from the lower layers; and the law of rarefaction will be the same as for air."

To test this hypothesis Perrin prepared a uniform suspension of purified gamboge in water by means of fractional centrifuging. The results confirmed the hypothesis. With gamboge particles 0.3μ in diameter a rise of 30μ was sufficient to lower the concentration to a half of its value, 30μ in the gamboge suspension being equivalent to 6 kilometers in the air.[4] Satisfactory results have also been obtained by Zangger[5] for drops of mercury, by Brillouin[6] for gamboge in glycerol solutions having a viscosity 160 times that of water, and by Iljin.[7] This cannot be true over any appreciable range because it would mean that the concentration would drop to one-billionth in a rise of about a millimeter, which would mean that no colloidal solution would appear uni-

[1] Sitzungsber. Akad. Wiss. Wien., **56** II, 116 (1867).

[2] Zsigmondy: Kolloidchemie, 18 (1912).

[3] Brownian Movement and Molecular Reality, 22 (1910).

[4] Perrin: Brownian Movement and Molecular Reality, 43 (1910).

[5] Zeit. Kolloidchemie, **7**, 216 (1911).

[6] Ann. Chim. Phys. (8) **27**, 412 (1912).

[7] Zeit. phys. Chem., **83**, 592 (1913).

form. It has been suggested by Burton that the concentration increases with increasing depth only up to about a certain value and then remains practically constant.

Einstein[1] assumes that suspended particles will behave exactly like dissolved particles, exerting an osmotic pressure and diffusing through the solvent.[2] Instead of the van't Hoff expression that the osmotic pressure, P, of a dissolved substance is given by the equation

$$PV = nRT$$

Einstein deduces the equation

$$PV = \frac{n}{N} RT,$$

where n is now the number of suspended particles and N is Avogadro's constant or the actual number of molecules in a gram-molecule. Following this up he deduces for the rate of diffusion the equation

$$D_x = \sqrt{\frac{RT}{N\pi} \frac{t}{3r\eta}}$$

where D_x is the displacement in a given direction, t is the time, R is the gas constant, T the absolute temperature, N is the Avogadro constant, r is the radius of the particles and η is the viscosity of the liquid. This has been confirmed quantitatively by Perrin who gets a mean value[3] of about 68×10^{22} for N. In regard to this he says:[4] "Thus the molecular theory of the Brownian movement can be regarded as established experimentally, and it becomes very difficult to deny the objective reality of molecules. At the same time we see the law of gases, already applied by van't Hoff to dilute solutions, extended to uniform emulsions. The Brownian movement offers us, on a different scale, the faithful picture of the movements possessed,

[1] Drude's Ann., **17,** 549 (1905); **19,** 280, 371 (1906). See also Smoluchowski: Ibid., **21,** 756 (1906).

[2] It must be remembered that Einstein has ignored all adsorption of the liquid by the suspended particles. He did the same thing when deducing a formula for the viscosity of colloidal solutions and came to the erroneous conclusion that the viscosity depends only on the volume and not on the size of the suspended particles.

[3] Perrin: Die Atome, 123 (1914).

[4] Perrin: Brownian Movement and Molecular Reality, 46 (1909).

for example, by the molecules of oxygen dissolved in the water of a lake, which, encountering one another only rarely, change their direction and speed by virtue of their impacts with the molecules of the solvent.

"It may be interesting to observe that the largest of the granules, for which I have found the laws of perfect gases followed, are already visible in sunlight under a strong lens. They behave as the molecules of a perfect gas, of which the gram-molecule would weigh 200,000 tons.

"I add lastly that all the measurements detailed in this paragraph have been made on dilute emulsions, which in the parts richest in granules only contain a thousandth part of resin, and where the osmotic pressure does not reach a thousand millionth of an atmosphere."

If we substitute four times the amplitude for $D_x (D_x = 4A)$ in Einstein's formula, t will be the time required for the particle to make one complete oscillation.[1] Einstein's formula therefore becomes

$$(4A)^2 = \frac{\pi RT}{N} \frac{t}{3r\eta}$$

If we are considering particles of the same size in various liquids we may write the equation $A^2 = k.t/\eta$ if we are working at constant temperature. "Since, by the kinetic theory, the average kinetic energy of a particle is the same as the average kinetic energy of a molecule, and the molecules of all fluids at the same temperature have the same average kinetic energy, we should expect the average velocity of all the particles to be the same, provided their masses are the same, whatever the liquid in which they are moving." Einstein's formula therefore leads to the set of relations: $A\eta = \text{const.}$; $D_x = \sqrt{T/\eta}$ and $D_x/\sqrt{t} = \text{const.}$

As has been pointed out, Svedberg had discovered independently that the product of the amplitude into the viscosity was a constant at constant temperature. Exner[2] found that the ratio of displacements at 20° and 71° is 1:1.6 while the ratio of the corresponding values of $\sqrt{T/\eta}$ for water at these two tempera-

[1] Burton: The Physical Properties of Colloidal Solutions, 76 (1916).
[2] Burton: The Physical Properties of Colloidal Solutions, 77 (1916).

tures is 1:1.7. Seddig[1] has shown by means of a photographic method in conjunction with the microscope, that finely divided cinnabar in water obeys Einstein's formula, the greatest departure from the theoretical value being 6 percent.

Chaudesaigues,[2] working with an emulsion of gamboge, varied the viscosity of a solution by adding sugar. In this way he carried out observations on two solutions containing the same-sized particles at the same temperature, the viscosities of which were in the ratio 1:4 and found that the motion was twice as fast in the less viscous solution as it was in the solution of higher viscosity. Chaudesaigues observed the velocities of particles of gamboge with radii respectively 4.5×10^{-5} cm and 2.3×10^{-5}, practically a ratio of 2:1, and found that these velocities varied inversely as the square of the radii. He also observed the distances described by 50 grains, each of radius 2.13×10^{-5} cm during successive intervals of 30 seconds each and obtained the following results: on the average the particles moved

6.7, 9.3, 11.8 and 13.95 microns in

30, 60, 90 and 120 seconds. The square roots of the times are proportional to the numbers,

6.7, 9.46, **11.6** and **13.4**, giving an ideal confirmation of this point.

It was first pointed out[3] by Smoluchowski[4] that we should expect to have the Brownian movements in gases as well as in liquids and he quotes from Bodaszewski[5] and O. Lehmann[6] as to the dancing movements executed by the particles of fumes of ammonium chloride, acids, phosphorus, etc. which they compared to the Brownian movements in liquids and interpreted as molecular movements.[7] The formulas of Einstein and Smoluchowski are based on the Stokes-law, which does not hold for gases under low pressure where the mean free path of the gas molecules

[1] Phys. Zeit., **9,** 465 (1908).

[2] Comptes rendus, **147,** 1044 (1908).

[3] Burton: The Physical Properties of Colloidal Solutions, 85 (1916).

[4] Drude's Ann., **21,** 756 (1906).

[5] Kosmos, **7,** 177 (1882); Beibl., **8,** 488 (1883).

[6] Molekularphysik, II, **5.**

[7] "The sun," says Daniel Culverwell, "discovers atoms, though they be invisible by candle light, and makes them dance naked in his beams."

is large relatively to the radius of the particles. Ehrenhaft[1] was the first to carry out direct measurements on the Brownian movement of particles in gases. He found that, as theory predicts, there is a much livelier motion in gases than in liquids; at the same time the action of gravity in causing vertical descent of the particles is also much more apparent in gases than it is in liquids. For comparatively large particles in the smoke of cigars and cigarettes and in the fumes of ammonium chloride, he observed an undoubtedly zigzag Brownian movement, while with smaller particles obtained by a spark discharge between zinc, platinum, or silver electrodes, Ehrenhaft concluded that he has proved without a doubt the existence of a motion in gases completely analogous to the Brownian movement in liquids.

It is more difficult to recognize this motion in gases on account of disturbing convection currents and the action of gravity. For the heavier particles, the velocity due to the force of gravity completely overshadows that due to the molecular shocks, while the opposite is the case with the very small particles. In Table XLI are given the velocities impressed by molecular shocks and by the force of gravitation, respectively, on silver particles of

TABLE XLI.—BROWNIAN MOVEMENTS IN GASES

Radius of silver particles	Velocity due to molecular shocks	Velocity due to gravity
$1\mu\mu$	63.0μ/sec.	$1.2\mu\mu$/sec.
$5\mu\mu$	28.0μ/sec.	$30.0\mu\mu$/sec.
$10\mu\mu$	20.0μ/sec.	$120.0\mu\mu$/sec.
$50\mu\mu$	8.9μ/sec.	3.0μ/sec.
$100\mu\mu$	6.3μ/sec.	12.0μ/sec.
$500\mu\mu$	2.8μ/sec.	300.0μ/sec.
1μ	2.0μ/sec.	1200.0μ/sec.

various sizes (density 10.5). These numbers show that when we reach particles having diameters of the order of the wave-length of light the two velocities do not differ materially. As we deal with smaller particles, the velocity induced by gravity soon becomes negligible, while with particles increasing above 0.1μ, the motion due to gravity soon dominates the situation. This is

[1] Sitzungsber. Akad. Wiss. Wien., **116** II*a*, 1139 (1907).

in keeping with what Ehrenhaft found. Particles, the linear dimensions of which were of the order of the size of the mean free path of gas molecules (0.1μ), and somewhat larger particles, fall in a zig-zag line, the velocity due to gravitation being greater than that due to molecular shocks. Particles, which are near the limit of visibility in the ultra-microscope ($1\mu\mu$), are in such lively molecular motion that the vertical gravitational velocity is completely masked. Ehrenhaft viewed silver particles that remained in lively motion in the air of his ultra-microscope cell for some thirty minutes. His measurements on the cigarette smoke particles gave a mean velocity of 25μ/sec. and on the smaller particles of silver, 46μ/sec.

Much interesting work has been done in this field by De Broglie.[1] Both Ehrenhaft and De Broglie have found that these silver particles suspended in air, are charged and, by measuring the velocity impressed on them by a known electric field, have come to the conclusion that the charge is that of one electron. The values that they find for this charge,[2] e, are respectively 4.6×10^{-10} and 4.5×10^{-10} electrostatic units. Wells and Gerke[3] have measured the velocity of smoke particles in an electrical field and have determined the size of the particles from the resulting data.

It seems to be accepted pretty generally that the work of Perrin, Svedberg, and others has established the practical continuity between suspended particles and dissolved substances; but this seems to be an overhasty conclusion. The molecular weight of a dispersed substance, as calculated from any of Einstein's formulas means something entirely different, if it means anything at all. We can determine the molecular weight of liquid benzene approximately from a measurement of the surface tension; but it is absurd to say that suspending fine drops of benzene in water causes the molecular weight of benzene to be equal to 200,000 tons.[4] We are talking about entirely different things in the two cases. What we mean is that dissolved ben-

[1] Comptes rendus, **146,** 624, 1010 (1908); **148,** 1163, 1315 (1909).

[2] See also Millikan: Phil. Mag. (6) **19,** 209 (1910).

[3] Jour. Am. Chem. Soc., **41,** 312 (1919).

[4] Such a hypothetical gas would have a density roughly a million times that of metallic copper.

zene has a molecular weight of 78, and that liquid benzene suspended in water behaves or may behave as if it were a dissolved substance having a molecular weight of 200,000 tons, more or less. As a matter of fact the experiments bring out clearly the enormous difference between a solution and a suspension.

The safe ground to take is: that the Brownian movements are due to the incessant movements of the molecules of the fluid; that the Brownian movements tend to make finely-divided, suspended particles distribute themselves uniformly throughout the liquid; that the uniform distribution is affected by the force of gravity as in the case of a gas; and that the Brownian movements, though causing diffusion, give rise to no appreciable osmotic pressure.

Very finely divided particles (less than 0.5μ for instance) will be kept in suspension indefinitely by the Brownian movements, so long as the particles remain finely divided. If, however, two or more particles agglomerate or coalesce, the force of gravity may cause the particles to settle to the bottom of the containing vessel.

CHAPTER V

COALESCENCE

Coalescence of Liquids

If two small drops of a pure liquid are brought in contact, they run together and form a larger drop. The two small drops are therefore instable with respect to a larger drop. Consequently we should expect the small drop to distill over to, and condense on, a larger drop. This is equivalent to saying that the greater the curvature of the drop, the higher the vapor-pressure. This conclusion was drawn by Lord Kelvin, then William Thomson,[1] many years ago. He reached his conclusion in a slightly different way. If we have a capillary tube dipping into a liquid, the whole being in a closed vessel containing only the liquid and its vapor, the raised liquid surface in the capillary must be in equilibrium with the main surface of the liquid if the system is all at the same temperature. The pressure of the vapor varies, however, at different levels in consequence of gravity. Consequently the concave surface of the liquid meniscus must have a lower vapor-pressure than the plane surface of the liquid. The converse must also be true that the convex surface of a drop must have a higher vapor-pressure than the plane surface of the liquid. This difference will be greater the greater the curvature of the surface or, in other words, the smaller the drop. The actual difference in vapor pressure between the highly curved surface in a capillary tube and the nearly plane surface in a wide vessel is very small. It amounts to one-thousandth of the vapor-pressure in a capillary tube in which water would rise thirteen meters.

Lord Kelvin[2] considered that this theory, originally due to Laplace, is applicable to cases in which the radius of curvature is

[1] Phil. Mag. (4) **42,** 448 (1871).
[2] Ibid. (4) **42,** 451 (1871).

as small as 1.2μ; but he thinks that we are not entitled to push it much further. Consequently he believes that the formulas he has deduced are not applicable to the vapor pressures of moisture retained by such substances as cotton cloth and oatmeal at temperatures far above the dewpoint of the surrounding atmosphere. He believes, however, that the difference is quantitative and not qualitative; that the adsorption of vapor by fibrous and cellular organic structures is a property of matter continuous with the adsorption of vapor into a capillary tube.

The converse of the theory is also true that liquid will distill into a capillary tube closed at the lower end until the height of the meniscus above the level of the liquid is the same as the height to which the liquid would have risen in the capillary tube if the lower end had been open. Bacon[1] has done the experiment successfully with ether, though the rate of distillation is very low.

The rate at which small drops coalesce depends on the mobility of the liquid. With viscous liquids such as cooling lavas or slags, we know that we get all sorts of phenomena which do not correspond to equilibrium relations, and it is probable that jellies are rarely in true equilibrium.

Coalescence of Solids

While it is perfectly familiar to all of us that two small drops of a pure liquid will coalesce readily to form a larger drop, all our ordinary experience is the other way in regard to solids and yet, theoretically, finely divided solids behave like finely divided liquids in many respects. A very finely divided powder must have a higher vapor-pressure, a lower melting-point, and a greater solubility[2] than the same substance in a more coarsely crystalline form. When yellow phosphorus is placed in a tube, the air removed, and the tube then sealed, it is said by Herman[2] and by J. Lawrence Smith[3] that crystals form in a short time on the walls of the tube and may grow to a diameter of 3–5 mm in the course of a month or six weeks. Crystals of iodine having a diameter of 2–3 mm were kept in the dark for eight years,

[1] Phys. Rev., **20,** 1 (1905).

[2] Ostwald: Zeit. phys. Chem., **35,** 495 (1900).

[3] Jour. Chem., Soc., **27,** 869 (1874).

the temperature varying from 0° to 24°. At the end of that time von Jonstorff[1] found that the smaller crystals had mostly disappeared and that the crystals were now about 4–5 mm in diameter. Hautefeuille and Perrey[2] found that at a dull red heat hydrochloric acid gas at a pressure of three atmospheres causes amorphous alumina to change into corundum, titania into anatase and zirconia into a crystalline form. The crystallization of the alumina is believed to be due to the successive formations and decompositions of an aluminum chloride. Emden[3] has shown that ice grains as large as hazel nuts may be grown from snow slush with original small ice nuclei, kept in sealed vessels for several weeks at a constant temperature of 0°.

Pawlow[4] states that crystals of salol which were 2μ in diameter melted 1.1° lower than crystals 40μ in diameter. Comparing a fine dust of less than 2μ diameter with crystals 0.5–2.0 mm diameter, differences of 4°–7° were obtained with salol, antipyrin, and phenacetin; but it seems probable that part of these differences is due to impurities and part to experimental error.

Hulett[5] found practically no difference for the solubility of calcium sulphate in water until the radius of the crystals was less than 2μ. Changing from 2μ to 0.3μ caused an increase in solubility of nearly 20 percent. A coarsely crystalline barium sulphate (1.8μ) was soluble 2.29 mg per liter at 25°. When ground in an agate mortar to 0.1μ the solubility rose to 4.5 mg per liter. The corresponding figures with natural barytes were 2.38 mg and 6.18 mg. Red mercuric oxide has a solubility of 50 mg per liter at 25°; when ground to a fine powder the color becomes yellow and the solubility increases to 150 mg per liter. Jones and Partington[6] made conductivity measurements on saturated gypsum solutions. They found no variation with size of crystals when the radius exceeded 50μ.

This parallelism between small grains and small drops makes one wonder whether the apparent failure of solid particles to

[1] Ber. deutsch. chem. Ges., **10,** 866 (1877).
[2] Comptes rendus, **110,** 1028 (1890).
[3] Von Engeln: Am. Jour. Sci. (4) **40,** 461 (1915).
[4] Zeit. phys. Chem., **65,** 1 (1908); **68,** 366 (1909).
[5] Ibid., **37,** 385 (1901).
[6] Jour. Chem. Soc., **107** II, 1019 (1915).

coalesce may not be due to experimental error. If we precipitate copper electrolytically on copper, we get a mass which does not differ materially in properties from cast copper having the same size of crystals.[1] The successive layers of copper coalesce to a uniform mass. On the other hand if we electroplate nickel on nickel without taking special precautions, we get a film of nickel which does not adhere. The reason for this is that the original nickel had an oxide film over the surface and the electrolytically precipitated nickel never really came in contact with the nickel electrode. If the oxide film is removed, the plating of nickel on nickel[2] is as simple as the plating of copper on copper. A silver halide adheres well to a silver anode if the conditions are such that the halide is formed in actual contact with the metal.[3]

If a plate were broken without chipping, the two pieces would fit together perfectly and should cohere, showing no signs of a break. This does not happen because of the film of condensed air which acts as an elastic cushion and keeps the two parts from actually being brought in contact.[4] A corollary from this is that if one were to break a plate in an absolute vacuum and were to bring the pieces together in the same vacuum, the plate should theoretically be as good as new. This is not likely to happen practically, because we cannot get an absolute vacuum. If we heat the fragments of any broken object, several things happen. At the higher temperature less gas is adsorbed and it is held less firmly. The solid is likely to become more malleable and it is therefore easier to make contact at a number of points. All chemists know that it is easy to make two glass rods unite at temperatures at which the glass is still very viscous. It may be urged that glass, at those temperatures, is unquestionably a liquid and not a solid. This criticism does not apply to platinum. To weld platinum it is only necessary to put two clean pieces of platinum in contact, to heat them to a moderate temperature far below the melting-point of platinum, and to give them a light tap with a hammer. Since the object in these cases

[1] Bennett: Jour. Phys. Chem., **16,** 294 (1912).
[2] Snowdon: Jour. Phys. Chem., **10,** 134 (1906).
[3] Reedy: Am. Jour. Sci. (4) **40,** 407 (1915).
[4] See Breuer: Kitte und Klebstoffe, 23 (1907).

is to bring two like surfaces into intimate contact, it is easy to see why clean surfaces are essential when soldering or brazing metals, and why it is important to use a flux. When iron is treated with sodium amalgam as a preliminary to dry-gilding,[1] part of the effect of the sodium amalgam is to clean the surface of the iron. Cold sodium cuts readily while warm sodium sticks to the knife.[2]

In some cases two surfaces will unite fairly readily. This is very noticeable with unvulcanized rubber from which it should follow that vulcanized rubber adsorbs air much more strongly. I do not know of any experiments along this line. Willows and Hatschek[3] point out that copper can be polished to such a degree that a cube of this metal will support eleven others merely placed in contact. This means that 1 cm^2 of surface carries a mass of copper 11 cm long and 1 cm square, a weight of about 98 grams. Polished plane surfaces of glass are apt to stick together. Usually this is to be avoided; but Parker and Dalladay[4] have taken advantage of this property. Glass surfaces can be polished without difficulty so as to be so nearly plane or so nearly of the same curvature that they show less than one interference fringe per inch when placed together and examined by light reflected from the interfaces. These surfaces may be brought into optical contact so that the two pieces of glass act optically as if they were one block by applying a pressure of several pounds per square inch. The two pieces can, however, be separated easily by sudden heating or cooling, by a shearing force, or by the application of liquids which creep in between the surfaces. By selection of the proper temperatures and pressures it has been found possible to weld two such pieces. It was found essential that the temperature at which union took place should not only be far below the melting-point of the glasses to be joined, but also below the annealing temperature, for even at that temperature a very slight strain would cause deformation of worked glass surfaces. At 60° below the annealing temperature it was found that two pieces of glass in optical contact would unite within an

[1] Kirchman: Jour. Chem. Soc., **26,** 418 (1873).
[2] McDonald: Chem. News, **97,** 73 (1908).
[3] Surface Tension and Surface Energy, 8 (1915).
[4] Engineering, **103,** 23; Jour. Franklin Inst., **183,** 369 (1917).

hour and that any slight deformation produced by the compression could be remedied by a few strokes of the polishing tool.

Mr. Jerome Alexander has called my attention to the fact that freshly split pieces of mica can be made to coalesce by pressing them between the fingers. After they have been exposed to the air for five or ten minutes, it is impossible to make them unite in this way. This is undoubtedly due to the formation of a surface film, because Lord Rayleigh[1] found that freshly split surfaces of mica attract to themselves at once a coating of moisture which is replaced or supplemented in a few hours by a layer of grease. The fresh surface conducts electricity, while an old surface, in which the moisture has presumably been replaced by grease, insulates well. I have been told that some of the electrical companies make mica blocks by compressing scrap mica; but I do not know any of the details of the process. Horn waste and tortoise-shell waste may be worked up into solid masses by high pressure and moderate heat.[2]

While it is not possible as a usual thing to mend a broken object by pressing the two pieces together at ordinary temperatures, Spring[3] has shown that powders may be welded into massive blocks by the use of sufficiently high pressures. This means that the pressure has been sufficient to squeeze out the air films coating the powders.

Since solids will coalesce when heated and subjected to pressure, there is no reason why some solid powders should not coalesce to some extent under the influence of gravity when heated. This is known as sintering or sometimes as fritting. The two terms are not distinguished as sharply as they might be.[4] Sintering should be used when a powder coalesces without melting or with but slight fusion, so that the product is still granular and more or less porous. Fritting should be used when the fusion is quite marked and the product is distinctly glassy. The forma-

[1] Scientific Papers, **3,** 523 (1902).

[2] Koller: The Utilization of Waste Products, 62 (1915).

[3] Bull. Acad. roy. belg. (2) **49,** 323 (1880); Ann. Chim. Phys. (5) **22,** 170 (1881); Ber. deutsch. chem. Ges. **15,** 395 (1882); Bull. Soc. chim., Paris, (2) **40,** 520 (1883); Friedel: Ibid. (2) **39,** 626; **40,** 526 (1883); Jannetz, Neel and Clermont: Ibid. (2) **40,** 51 (1883); Tammann: Zeit. Elektrochemie, **15,** 447 (1909).

[4] Percy's Metallurgy: Fuel, 46, 280 (1875).

tion of bricks and pottery involves sintering; the materials for glazes are fritted. There has been some question whether sintering could take place without at least incipient fusion. Lucas[1] maintained that it was a property of amorphous substances only, in which case it would be nothing more than the slow and partial coalescence of very viscous drops. Day and Allen[2] found that powdered glasses sinter slowly or rapidly several hundred degrees below the melting temperature of crystals of the same composition. The first traces of sintering appear earlier the finer the powder and the slower the heating. There is no doubt that the sintering of powdered glasses is due to flow in a supercooled liquid and that it is a phenomenon of viscosity and surface tension. Powdered crystalline feldspars do not sinter readily below their melting temperature and, at first, Day and Allen were inclined to suspect that pure, dry, stable crystals would not sinter at all. Their final experiments, however, showed that the purest crystalline feldspar which they could prepare still sintered, though very slowly. Kohlschütter[3] found that porous silver obtained by reducing silver salts in different ways, sintered at temperatures from 200°. Instead of concluding that a crystalline substance can sinter, he drew the surprising conclusion that Lucas was right and that therefore the degree of sintering of the silver was a measure of the amount of amorphous silver present, even though he points out the relation between the porosity and the sintering.

Other things being equal the contraction or sintering is greater the higher the temperature, and consequently the higher the temperature the denser the solid. Bricks are less porous the higher the temperature of burning. Of course if the temperature is reached at which vitrification takes places a new phenomenon occurs. Magnesia is more dense the higher it is heated[4] and so is lime.[5] While it is unquestionably true that sintering will take place less readily with a pure crystalline substance than with an amorphous one or with one containing impurities which

[1] Zeit. phys. Chem., **52,** 327 (1905).
[2] Carnegie Inst. Pub., **31,** 59 (1905); Zeit. phys. Chem., **54,** 39 (1906).
[3] Liebig's Ann., **398,** 37 (1913); Reedy: Am. Jour. Sci. (4) **40,** 407 (1915).
[4] Ditte: Comptes rendus, **73,** 270 (1861); Moissan: Ibid., **118,** 506 (1894).
[5] Wright: Zeit. anorg. Chem., **68,** 397 (1910).

lower the melting-point[1] and cause a portion of the mass to soften long before the whole mass is fused, this does not prevent sintering occurring with perfectly pure crystalline substances. The technical advantage of impurities is shown in the case of magnesia.[2] The crystalline Styrian magnesite is less pure than the amorphous Grecian magnesite, containing more iron. It therefore sinters more readily and at a lower temperature. It is often preferred for this reason to the purer Grecian magnesite, which must either be burned at a higher temperature or must have some bonding material added which will cause sintering at lower temperatures. Of course, the material which sinters at a low temperature will not stand up at so high a temperature as a purer substance which has been shrunk in an electric furnace at a higher temperature.

The sintering of tungsten[3] and of tantalum[4] powder is a technical process carried on far below the melting-point of tungsten, and not depending, so far as we know, on the presence of impurities, though these may be present. Another interesting case of sintering occurs in the gold assay.[5] After parting, the cornets are of a dull brown color and very friable. When annealed at a bright-red heat they sinter very much and become a pure gold-yellow color. This has been studied in detail by Hanriot[6] who took an alloy containing four parts of silver to one of gold and dissolved the silver with nitric acid. The gold was left in a spongy brown form which decreased rapidly in bulk on heating and became gold color. Wöhler[7] has shown that the glowing of heated chromic oxide jellies is the result of rapid sintering and not of the formation of an allotropic modification.

Soot becomes sandy if heated too long or too hot. The density of red phosphorus depends on the heat treatment. Many precipitates sinter or agglomerate on standing, though the change is not usually called that. The agglomeration is often accompanied

[1] Endell: Silikat-Zeitschrift, **2,** 1, 25 (1914).

[2] Havard: Refractories and Furnaces, 89 (1912).

[3] Ruff: Zeit. angew. Chem., **25,** 1889 (1912).

[4] Siemens and Halske: Jour. Soc. Chem. Ind., **23,** 206 (1906).

[5] Percy's Metallurgy: Silver and Gold, 268 (1880).

[6] Comptes rendus, **151,** 1355 (1910); **152,** 215 (1911); cf. Prat: Ibid., **70,** 841 (1870).

[7] Zeit. Kolloidchemie, **11,** 241 (1912).

by increased resistance to chemical action. Strongly heated lime reacts very slowly with carbon dioxide.[1] After short ignition, silica dissolves in a boiling solution of potassium or sodium carbonate, but does not if ignited for a long time. Freshly precipitated arsenic sulphide gives off much hydrogen sulphide when boiled with water; but does not after being heated[2] at 125°. Pulverulent iron burns in the air while massive iron does not. The action of alkali on hydroxides, and of gelatine and ammonia or potassium bromide on silver bromide is decreased enormously if the precipitates are allowed to stand over night. Holmes and Fall[3] have made a quantitative study of the change in peptizability of ferric arsenate, so-called, with time of standing.

A plastic substance is one which can be moulded by pressure.[4] This connotes that any break due to the deformation is self-healing. A mobile liquid is not plastic, because it will not retain its shape. With increasing viscosity a liquid becomes plastic. Molasses candy is plastic until it crystallizes. Semifused glass is plastic. The time factor may be important. Sealing-wax is brittle if the pressure is applied rapidly; but is plastic if the rate of deformation is low. Since metals and other solids coalesce under high pressure, there is no reason why they should not be plastic under the same conditions, as indeed they are. We make use of this property when squirting metals into rods or pipes. Under high pressure ice is also plastic. It has been claimed by Spring[5] and by Kahlbaum[6] that solids become almost like mobile fluids under high pressure; but it seems to have been proved conclusively by Spezia[7] that this is not true when the pressure is uniform and that the apparent fluidity occurs only when there is a shearing force. The question of unequal pressures has been

[1] Raoult: Comptes rendus, **92,** 189 (1881); Sosman, Hostetter and Merwin: Jour. Washington Acad. Sci., **5,** 563 (1915).

[2] Rammelsberg: Jour. Chem. Soc., **26,** 242 (1873); cf. Laufer: Ber. deutsch. chem. Ges., **11,** 60, 935 (1878).

[3] Jour. Am. Chem. Soc., **41,** 713 (1919).

[4] Duff: A Text-Book of Physics, 4th Ed., 119 (1916).

[5] Bull. Acad. Soc. belg. (2) **49,** 364 (1880).

[6] Verh. Naturforscherges. Basel, **15,** 14 (1903).

[7] Atti. Accad. Sci. Torino, **45,** 525 (1911); **46,** 682 (1912).

discussed in some detail by Johnston.[1] Iron filings in presence of a magnet might be considered a special case of plasticity, though not one of any great interest. Another special case of partial plasticity is the mineral itacolumite[2] which is said to have something akin to a series of ball-and-socket joints. Each ball and socket does not admit of a great play, and is not smooth and perfect like that of the joint of a limb. The stone is built up of grains and masses of grains, which are loosely coherent and form irregular cavities in which are engaged projecting parts of other grains or masses of grains of sand, susceptible of a slight motion in the cavity, in some cases in one direction, and in others in several or in all directions. This freedom of motion is of the true quality of a ball-and-socket joint. Perhaps it would be better to call this mineral flexible rather than plastic.

Between the extreme cases of a solid such as a metal and a liquid such as glass or molasses candy, we have the intermediate case of putty which is whiting and oil, or a solid with a liquid film around it. If a liquid is adsorbed strongly by a solid, thin films of the liquid will hold the solid particles together, while still permitting them to move relatively to one another. The tendency of liquid surfaces to coalesce causes any break to heal. A liquid film may therefore act as a bond for solids and may make the mass plastic. Oil is used as a binder in roads and to make putty out of calcium carbonate. Everybody knows that dry sand cannot be moulded whereas wet sand can. Fondant consists of very small crystals of sugar made plastic by a syrupy film of invert sugar and water. Plastic dynamite is made by adding three parts of nitroglycerine[3] to one part of diatomaceous earth. Bingham[4] has made a preliminary study of the concentration at which plasticity begins or ends. If a finely powdered solid is added to a liquid, the viscosity of the liquid is increased or the fluidity, which is the reciprocal of the viscosity, is decreased. The fluidity was calculated from the rate of flow of the liquid through a viscosimeter. At temperatures between 25° and 60°

[1] Jour. Am. Chem. Soc., **34,** 788 (1912); Johnston and Adams: Am. Jour. Sci. (4) **40,** 351 (1915).

[2] Wetherill: Chem. News, **22,** 266 (1870).

[3] Thorp: Outlines of Industrial Chemistry, 3d Ed., 482 (1916).

[4] Am. Chem. Jour., **46,** 278 (1911); Jour. Franklin Inst., **181,** 845 (1916).

the fluidity dropped to zero at the same concentration, so the concentration for zero fluidity is independent of the temperature over the range studied. With infusorial earth in water, zero fluidity was reached at a volume concentration of about 13 percent solids; with China clay at about 4 percent; with the graphite used in Acheson's aquadag zero fluidity was reached at a volume concentration of about 5.5 percent graphite; and with an unspecified clay at about 19.5 percent clay. With infusorial earth in alcohol, zero fluidity was reached at a volume concentration of about 12 percent solids. The mixtures having zero fluidity are not stiff and will not maintain their shape. At higher concentrations there is a change from viscous flow to plastic flow. The distinction made by Bingham is that with viscous flow any shearing force—no matter how small—will produce permanent deformation, whereas, in the case of plastic flow, it is necessary to use a shearing force of finite magnitude in order to produce a permanent deformation. It seems reasonable to assume that we reach zero fluidity when liquid enough is added to the solid to begin to scatter the particles, in other words, when about enough liquid is added to fill the voids. This is true in one case studied by Bingham. The clay referred to contained 81.6 percent voids and required 80.5 volume percent of water to bring it to zero fluidity. The two values would only be identical in case the volume of the adsorbed water just equalled the volume of the adsorbed air. Of course this very important generalization of Bingham's must be tested in more cases before it can be considered as definitely established; but it is so obvious, after it has been pointed out, that it must be approximately true. This discovery of Bingham's may be of distinct importance in the paint industry. The oil requirement for a given pigment is a very arbitrary amount and experts often differ widely in their values. Reproducible figures could be obtained if in each case there was determined the amount of oil necessary to give zero fluidity. Since this is more oil than painters wish to use, it might be advisable to adopt as the standard, some definite fraction of the amount of oil necessary to produce zero fluidity.

Emley[1] has made some determinations on the viscosity of lime pastes. Judging from the diagram given, the viscosity

[1] Trans. Am. Ceramic Soc., **15**, 401 (1913).

would become infinite or the fluidity zero when there was about 50 percent of hydrated lime in the paste. Since Emley used the Clark viscosimeter, one does not know to what extent his results are comparable with those of Bingham.

Since the concentration producing zero fluidity apparently depends on the volume of the voids, it is necessary to consider approximately what this may be. If equal spheres are taken and are piled so that each sphere is directly on top of another—minimum or cubical piling—the voids constitute theoretically about 48 percent of the whole, irrespective of the size of the spheres. If the spheres are piled so that each one rests equally on the four in the layer below—maximum or hexagonal piling—the theoretical percentage of voids is nearly 26, again irrespective of the size of the spheres. With solids of different sizes and different shapes, the voids may theoretically be made almost anything. If the solids have condensed air films round them so that they do not come actually in contact, the percentage of voids will go up with decreasing size of the solids. As a matter of fact, we have seen that the voids in carbon black may run up to 95 percent or thereabouts. If the air-adsorption were negligible and if the particles were cubes of the same size and arranged in an orderly fashion the voids would be practically zero. As a matter of fact round-grained water-worn sands have 2–5 percent less voids than corresponding sharp grains of sand[1] because the former pack better. The difference between the theoretical values and the actual values as found under certain experimental conditions is shown by the statement that large enough masses of equal-sized marbles cannot be poured or tamped into a large vessel so as to give less than 44 percent voids. Undoubtedly these would have jarred down in time so as to occupy a lesser volume; because this result comes very close to that required for cubical piling. The effect of moisture on sand is also unexpected at first.[2] Moist sand occupies more space and weighs less per cubic foot than dry sand. The explanation of this apparent anomaly is that a film of water coats each grain of sand and separates it from the adjacent ones. Since fine sand has a large number of grains and consequently more surface area, addition

[1] Taylor and Thompson: Plain and Reinforced Concrete, 174 (1912).
[2] Taylor and Thompson: Plain and Reinforced Concrete, 176 (1912).

of water to it causes a greater increase in bulk than in the case of coarse sand. If a small quantity of water is poured into a vessel containing dry sand, the friction of the particles keeps the volume from increasing; but the bulk increases if the moistened sand is dumped out and then turned back into the vessel with a shovel or trowel. The percentage of water by weight which will give the greatest volume—corresponding to the largest percentage of voids—varies with different sands from 5 to 8 percent.

Since the densest mixture occurs with particles of different sizes, it is important, in making concrete, to grade the materials so as to get the maximum density.[1] On the other hand for a sand filter the grains of sand should be of approximately the same size,[2] as otherwise the filter clogs too readily. The question has also been raised but not answered, as to what are the proper sizes for the balls in the ball mill. Since there should probably be more of the small balls than the large ones, the proper ratio cannot be obtained if only large balls are added as the others wear down.[3]

A number of curious things in regard to wetted sand have been pointed out by Osborne Reynolds.[4] If we have sand in maximum piling in a rubber bag and enough water to form a thin layer over the surface, squeezing the sand will necessarily cause it to expand or dilate, and the water will be sucked down into the dilated mass. We are familiar with this experiment in another form. The wet sand below high water mark is in the position of maximum piling. When one walks over this sand, the sand whitens momentarily and appears to dry around the foot. The sand is full of water, the surface of which is kept up to that of the sand by capillary attraction. The pressure of the foot dilates the sand and since the water does not suck up rapidly enough, the water level is lower in the dilated sand than before and consequently the sand appears dryer until more water has been brought up from below by capillary action. On raising the foot, the sand in and around the foot-print usually becomes wet momentarily, because the sand contracts when the shearing pressure is taken off and the excess of water is left momentarily on the surface.

[1] Upton: Materials of Construction, 304 (1916).
[2] Mendeleeff: Jour. Chem. Soc., **48**, 114; Lueger: Ibid. 48, 198 (1885).
[3] Chem. Met. Eng., **14**, 285, 292 (1916).
[4] Phil. Mag. (5) **20**, 469 (1885); Scientific Papers, **2**, 217 (1901).

In a filter press the solid to be filtered tends to go into cubical piling because that lets the water through most readily. If the crystals are displaced so that they pass into hexagonal piling, water will be set free. Hatschek[1] says in regard to this that it is a perfectly familiar fact that apparently dry cakes of calcium sulphate, for instance, which break with a clean fracture can be reduced to an almost liquid mass by mere shaking It seems probable that in quicksands the sand is in a state of cubical piling, making it possible for a man to sink in it and raise the water without raising the sand.

To show some of the phenomena due to dilatancy Osborne Reynolds took a thin, transparent, india-rubber balloon, filled it with about six pints of sand and water, and closed it so that it contained no air. There was more than enough water to fill the voids when the sand was at maximum density but not enough to fill them when the sand was at minimum density. When this rubber sack was laid on the table, the elasticity of the rubber gave it a rounded shape. The sand settled into the condition of maximum piling and there was consequently a layer of water above the surface of the sand. The bag can be squeezed and altered in shape as though it had no firmness, so long as the sand does not rise to the surface of the water. If the bag is placed between two vertical boards and squeezed, it changes shape at first apparently without resistance, but soon comes to a dead stop. Turning it on its side and laying a 56 pound weight on it produced no further change in shape; but on removing the weight the bag goes back to its almost rounded shape. If the bag is shaken slightly while it is being squeezed, the sand keeps at its densest and the bag can be pressed out until it is a broad flat plate. The bag is soft so long as it is squeezed; but if the pressure is removed, the elasticity of the rubber tends to draw the bag back to its rounded form. This dilates the sand and causes the excess of water to be sucked into the pores. So soon as there is no excess of water, no further change takes place and the bag remains a flat cake with peculiar properties. It yields at once to pressure on its sides, such pressure having nothing but the elasticity of the bag to overcome because pressure in that direction causes the sand to contract. It is perfectly rigid,

[1] Jour. Soc. Chem. Ind., **21**, 540 (1908).

however, to radial pressures because such pressures tend to dilate the sand still farther. When placed on its edge, it will hold up a hundred pounds. If, however, it is pressed sufficiently on the sides while holding up such a weight, all the strength vanishes and it is again a rounded bag of loose sand and water. By shaking the bag into a mould, it can be made to take any shape; then by drawing off the excess of water and closing the bag, the sand becomes perfectly rigid and will not change its shape unless the bag is torn. Since the sand is at its maximum density, no amount of shaking will produce a change. In this way bricks can be made of sand or fine shot with water in the thinnest india-rubber envelope and they will withstand as much pressure as an ordinary brick without change of shape.

The clay workers use the word plasticity in a special sense to denote that a clay is plastic and will burn to a coherent mass. From this point of view wet sand is not plastic because it falls to pieces when dried. To meet this definition we must have in the water some bonding material presumably in a gelatinous form. The film of water about the clay particles is usually assumed to be $50\mu\mu$ in thickness.[1] There is no difficulty in accounting for a gelatinous film.[2] Cushman[3] has shown that the cementing power of rock powders is due to the formation of gelatinous silica, ferric, oxide, etc. If we have a gelatinous film which is adsorbed strongly by the solid particles and which can take up and lose water, we shall have plasticity. In the case of clay the gelatinous material may be hydrous alumina, hydrous silica, or some intermediate composition. The difficulty, however, is to account for its remaining plastic after moderate drying and for its readsorbing water to form a gelatinous mass. This is probably due to the presence of some salt; but we do not know what salt and consequently we cannot tell why one clay is plastic and another not, and we do not know what we should add to the non-plastic clay to make it plastic. People have never studied the problem from a rational point of view.

From this study of coalescence we conclude that liquid drops

[1] Grout and Poppe: Trans. Am. Ceramic Soc., **14,** 73 (1912); Davis: Ibid., **16,** 19 (1914).

[2] Quincke: Drude's Ann., **7,** 74 (1902).

[3] Jour. Am. Chem. Soc., **25,** 451 (1903).

or solid grains will coalesce or agglomerate if brought into actual contact. To keep them from doing so we must have a surface film of some sort. Since this coalescence or agglomeration takes place spontaneously, work must be done on the liquid or solid to disintegrate it. It is easy to see that a film might keep drops separated and yet not break up a large drop into a lot of smaller ones. Dirty mercury will remain indefinitely as a single liquid mass so far as we know. If we disintegrate the mass by shaking, a film will form over each drop and will keep the drops from coalescing. This "flouring" of mercury, as it is called, is a distinct source of trouble when extracting gold by the amalgamation process. In most cases the film is oxide, chloride, or grease, though it may consist of oxides of other metals if one starts with an amalgam. Anything that will dissolve the surface film will cause the drops of mercury to run together. Treatment with potassium cyanide is therefore very effective. Emulsions of oil in water are obtained if some substance like sodium oleate is present to form a film over the drops of oil, thus keeping them from coalescing.[1] It is easy to see that the work necessary to break up a liquid or solid mass into drops or grains will be less if we add something to the solution which will lower the surface tension of the liquid or solid. In some cases water alone will cause the disintegration. With gelatine we get reversible disintegration at very moderate temperatures, say 30°; but cellulose requires a very much higher temperature. We do not know at all to what extent this matter of disintegration depends upon the structure; but a single illustration from the field of true solutions will show the possibility of such a factor. If we place a crystal of rock candy in cold water the crystal dissolves so as to keep its shape approximately. It grows smaller but does not fall to pieces. If we put a lump of sugar into cold water, the smaller crystals which act as binding material dissolve first and the lump disintegrates to a mass of grains.

Types of Precipitates

Sufficiently finely divided particles will be kept in suspension in a liquid indefinitely by the Brownian movements, provided coalescence and the resulting agglomeration are prevented.

[1] Cf. Donnan and Potts: Zeit. Kolloidchemie, **7**, 208 (1910).

Such a colloidal solution is called a sol. One may use the words hydrosol, alcosol, etc., to show that the dispersing liquid is water, alcohol, etc. When the colloidal particles agglomerate and precipitate, the precipitate is called a gel, or a hydrogel in case the dispersing liquid is water. The word gel is also used to include a jelly, which differs from a gelatinous precipitate in that there is no supernatant liquid when first formed. It is really the general term for a solid or semi-solid colloid. The change from a gel to a sol is usually called peptization, a term which we owe to Graham. The reverse change from sol to gel was called pectization by Graham; but this term has never become popular. A stable colloidal solution will consist of very fine particles kept from agglomerating by a protecting film[1] of some sort, electrification being equivalent to a film.[2] Small particles[3] may be obtained either by condensation from vapor or solution (usually called precipitation) or by disintegration of larger masses. The disintegration is often called peptization especially when done chemically, as opposed to mechanical or electrical disintegration. People have distinguished eight types of precipitates: crystalline; colloidal or non-settling; flocculent; curdy; sandy; gelatinous; jelly-like; fluid. A crystalline precipitate is one that is distinctly crystalline and settles rapidly, as when KOH is neutralized by H_2SO_4 or when moderately concentrated solutions of lead nitrate and potassium chromate are mixed. A non-settling precipitate may be anhydrous or hydrous; there is little or no agglomeration. A typical case is the precipitation of lead chromate from very dilute solutions of lead nitrate and potassium chromate.[4] A flocculent precipitate is obtained when a non-settling, non-gelatinous precipitate agglomerates to a bulky mass. It is easy to obtain a flocculent precipitate of silver chloride from suitable solutions of silver nitrate and potassium chloride. Haber and Oordt[5] call the precipitate of beryllium hydroxide flocculent; but I am not certain whether they are limiting the term sufficiently sharply. A curdy precipitate is obtained when a flocculent

[1] Cf. Höber: Physikalische Chemie der Zelle und der Gewebe, 233 (1914).
[2] Cf. Hardy: Proc. Roy. Soc., **86A**, 601 (1912).
[3] Freundlich: Kapillarchemie, 527 (1909).
[4] Free: Jour. Phys. Chem., **13**, 114 (1909).
[5] Zeit. anorg. Chem., **38**, 377 (1904).

precipitate agglomerates to a fairly dense mass. The typical case is, of course, the precipitation of caseine by acids, but a similar precipitate can be obtained with $AgNO_3$ and HCl. There is no sharp dividing line between a flocculent and a curdy precipitate. A sandy precipitate is obtained when a flocculent or a curdy precipitate agglomerates to a dense mass. The alumina from hot sodium aluminate in the Bayer process is a sandy precipitate.[1] A granular or sandy alumina is said to be precipitated by ammonia[2] at 66°. A gelatinous precipitate is always viscous; it involves agglomeration to a bulky form. Hydrous alumina and hydrous ferric oxide, when precipitated cold, are typical gelatinous precipitates. When a sparingly soluble salt is precipitated from very concentrated solutions we apparently always get a gelatinous precipitate. Thus gelatinous barium sulphate is obtained by mixing concentrated solutions of barium sulphocyanate and manganese sulphate,[3] and gelatinous calcium carbonate by mixing concentrated solutions of calcium chloride and sodium carbonate. The difference between a gelatinous precipitate and a jelly is that the liquid phase is visible as such in the case of the gelatinous precipitate and is not in the case of the jelly. A jelly is always hydrous, viscous, and bulky; it may consist of a number of coalescing drops or rods, in which case both phases are continuous; or it may consist of coalescing films, in which case we have a honeycomb structure, with water as the internal phase. A typical jelly can be obtained with sodium silicate and hydrochloric acid. A fluid precipitate is one which is too mobile to be classed as a gelatinous precipitate. Sodium phenolate or sodium oleate with an excess of HCl gives a fluid precipitate.

The mean mass of the crystals in a crystalline precipitate is given by the total weight of the precipitate divided by the number of crystals. Experimentally we find that the number of nuclei increases less rapidly than the concentration at first and more rapidly later. When very dilute solutions are mixed, the number of nuclei is so large relatively to the weight of the precipitate that the particles themselves are very small. With increasing

[1] Russ: Zeit. anorg. Chem., **41,** 216 (1904).
[2] Von Weimarn: Gründzüge der Dispersoidchemie, 67 (1911).
[3] Taylor: Chem. News, **103,** 169 (1911).

concentration we get increasing size of crystals for a while and then decreasing size, because the number of nuclei then increases more rapidly than the concentration. At very high concentrations a gelatinous precipitate is always obtained, as has been pointed out. It is possible that we have here the appearance of a viscous and instable second liquid layer; but this has not yet been proved. According to Clowes a jelly is formed when a viscous phase separates slowly in presence of a substance which tends to keep it dispersed.[1] To obtain large crystals one must have a solution so slightly supersaturated that no nuclei form spontaneously and that no branched crystals form in presence of a single crystal.[2] Von Weimarn[3] cites the case of a spring in which crystals of barium sulphate had grown 5 cm long! Geologists have prepared certain substances in distinct crystals by arranging for the slow diffusion of dilute solutions of two salts which form the desired substance by metathetical reaction. Johnston[4] has improved on the technique by allowing the two solutions to diffuse into a large vessel containing water, causing a further dilution. Dreaper[5] obtained distinct crystals by letting solutions diffuse through sand, the rate of diffusion being relatively slow on account of the capillary spaces. Holmes[6] obtained crystals of silver bichromate in flat needles one cm long by this method, substituting aluminum powder for sand. He filled a small test-tube full of N/10 potassium iodide, covered the mouth of the tube with gold-beater's skin, and immersed the tube in a small beaker containing a saturated lead acetate solution. At once an almost amorphous precipitate of lead iodide appeared on the under side of the membrane and in less than a minute crystals of lead iodide fell in a gleaming shower to the bottom of the test-tube. If the same solutions are mixed in a

[1] Cf. Hardy: Jour. Physiology, **24,** 167 (1899); Proc. Roy. Soc., **66,** 95 (1900); **87A**, 29 (1912); Holmes and Rindfusz: Jour. Am. Chem. Soc., **38,** 1970 (1916); Holmes and Fall: Ibid., **41,** 763 (1919).

[2] Cf. Hopkins: Am. Chem. Jour., **25,** 413 (1907); Bowman: Jour. Soc. Chem. Ind., **25,** 143 (1906); Hostetter: Jour. Washington Acad. Sci., **9,** 85 (1919); Moore: Jour. Am. Chem. Soc., **41,** 1060 (1919).

[3] Gründzüge der Dispersoidchemie, 55 (1911).

[4] Jour. Am. Chem. Soc., **36,** 16 (1914).

[5] Jour. Soc. Chem. Ind., **32,** 678 (1913)

[6] Jour. Phys. Chem., **21,** 709 (1917).

test-tube without using a membrane, a yellow powder is obtained and no easily recognized crystals. This method as developed by Holmes seems the most promising of any because it appears to give results with more concentrated solutions and would presumably work even better with more dilute solutions. Excessive supersaturation and consequently the formation of very fine precipitates can be obtained by using a solvent in which the resulting salt is practically insoluble.[1] It is easier to avoid supersaturation when the substance is more soluble. Thus one can get crystals of silver chloride without trouble from an ammoniacal solution.[2] The effect of other substances in the solution depends on their effect on the supersaturation and whether they are adsorbed by the precipitate.

If a precipitate forms in the presence of a substance which is adsorbed strongly by it, the adsorption will prevent the growth of the crystals and the precipitate will therefore come down in a finer state of subdivision. A typical case is the precipitation of silver bromide in presence of gelatine. The addition agents in electrolytic refining are substances which move to the cathode under the influence of the current and which are adsorbed strongly by the metal as it comes out. Barium sulphate precipitates in a finely divided form in presence of barium chloride[3] or potassium sulphate, both of which it adsorbs, and more coarsely crystalline in presence of sulphuric acid or hydrochloric acid.[4] Barium sulphate shows selective adsorption for its own ions, which accounts for the behavior of barium chloride[5] and potassium sulphate. The peptizing action of sulphate ions in sulphuric acid is cut down by the tendency of hydrogen ion to be adsorbed strongly. The precipitate is therefore more coarsely crystalline. The solvent action of hydrochloric acid is a factor in making the barium sulphate precipitate more coarsely crystalline.[6] The question has been raised whether the finest precipitates are crystalline or amorphous. Von Weimarn[7] calls them all crystal-

[1] Byk: Zeit. Elektrochemie, **13,** 38 (1907).
[2] Reinders: Zeit. phys. Chem., **77,** 696 (1911).
[3] Foulk: Jour. Am. Chem. Soc., **18,** 793 (1896).
[4] Mar: Jour. Chem. Soc., **60,** 1137 (1891).
[5] Weiser: Jour. Phys. Chem., **21,** 314 (1917).
[6] See also Osborne: Jour. Phys. Chem., **17,** 629 (1913).
[7] Zeit. Kolloidchemie, **3,** 166 (1908).

line; but he considers that liquids and gases are crystalline, which throws him out of court, because he is not using the word in the same sense as other people. A supercooled liquid like glass is amorphous in the ordinary sense of the term. Whether a precipitate is amorphous or not depends upon its being a supercooled liquid or not. Von Weimarn is undoubtedly right in saying that many precipitates are really crystalline, though they are classed as amorphous; but there is no question that there are amorphous precipitates.

In many cases there is a gradual change from an amorphous precipitate to a crystalline one on standing[1] and still more on heating.[2] At higher temperatures precipitates are less hydrous and tend to be more coarsely crystalline. There are no data in regard to a substance like sodium sulphate which is less soluble at 80° than at 40°. When barium sulphate is precipitated hot it does not run through the filter so readily as when precipitated cold. Other conditions being the same, a non-settling silver[3] is obtained by reduction with hydrazine at 16° and pulverulent silver by reduction at 80° to 90°.

Theory of Peptization

We find experimentally that certain solutions will peptize or disintegrate certain precipitates so that we get colloidal solutions. This is always the result of adsorption. Theoretically there are three possibilities. If an adsorbed film has a low surface tension on the water side and a high one on the other side, it will tend to scrunch up and to peptize the solid as internal phase. If the reverse is the case, the solid will tend to form the external phase. If the two surface tensions are practically equal, neither will prevail. Some adsorbed substances seem to have practically no peptizing action;[4] but these cases should be studied again in the light of what we now know about colloid chemistry. Tenta-

[1] Watson: Jour. Chem. Soc., **60**, 875 (1891); Gilbert: Jour. Phys. Chem., **18**, 86 (1914).

[2] Mouret: Comptes rendus, **123**, 54 (1896); Doelter: Zeit. Kolloidchemie, **7**, 29, 86 (1910); Galpin: Trans. Am. Ceramic Soc., **14**, 337 (1912).

[3] Gutbier: Zeit. Kolloidchemie, **4**, 308 (1909).

[4] Doyle: Jour. Phys. Chem., **17**, 390 (1913).

tive theories of peptization have been discussed by Lottermoser,[1] Jordis,[2] Mecklenburg,[3] and von Weimarn.[4] If we adopt Freundlich's view that adsorption always lowers the surface tension, a theory of peptization follows at once. We may have peptization by a liquid, by a non-electrolyte, by an adsorbed ion, by a salt, or by a peptized colloid. When a liquid is adsorbed by a solid, it will tend to peptize it and in some cases will do so. Water peptizes tannin, amyl acetate peptizes pyroxylin, and fused baths peptize metals. At higher temperatures the peptizing action increases, and we may get glass peptized by water[5] or vulcanized rubber by various organic liquids.[6] If the amount of substance peptized by a given mass of water under given conditions is fairly constant, it will look as though we were dealing with true solubility. In fact, data are to be found in the literature for the solubility of tannin in water.

There are a number of cases where mixed solvents will peptize a solid much better than either one alone—cellulose nitrates in ether and alcohol, caseine in pyridine and water,[7] and probably cinchonine in chloroform and alcohol,[8] as well as phloretine in ether and water.[9] The theory of this has not been worked out. Cellulose nitrate swells in alcohol and not in ether;[10] but it is not known whether this is universal. We do not know whether alcohol peptizes cellulose nitrate at higher temperatures. Zein is also peptized in mixed solvents.[11] Larguier des Bancels[12] claims that gelatine is peptized more readily by aqueous alcohol or aqueous acetone than by water alone.

[1] Jour. prakt. Chem. (2) **68,** 341 (1903); **72,** 39 (1905); **73,** 374 (1906); Zeit. phys. Chem., **62,** 371 (1908).

[2] Van Bemmelen Gedenkboek, 215 (1910).

[3] Zeit. anorg. Chem., **74,** 260 (1912).

[4] Lehre von den Zuständen der Materie, **1,** 160 (1914).

[5] Barus: Am. Jour. Sci. (3) **38,** 408 (1869); **41,** 110 (1891); (4) **6,** 270 (1898); **7,** 1 (1899); Phil. Mag. (5) **47,** 104, 461 (1899).

[6] Barus: Am. Jour. Sci. (3) **42,** 359 (1891).

[7] Levites: Zeit. Kolloidchemie, **8,** 4 (1911).

[8] Oudemanns: Jour. Chem. Soc., **26,** 533 (1873).

[9] Schiff: Zeit. phys. Chem., **23,** 355 (1897).

[10] Private communication from Professor Chamot.

[11] Galeotti and Giampalmo: Zeit. Kolloidchemie, **3,** 118 (1908).

[12] Comptes rendus, **146,** 290 (1911).

Relatively little work has been done on direct peptization by means of a dissolved non-electrolyte, but a good deal of stress has been laid on the cases where a non-electrolyte prevents the formation of a visible precipitate. A concentrated solution of sugar in water will prevent the precipitation of calcium silicate,[1] silver chromate, and silver chloride;[2] also of lime and of the hydrous oxides of copper[3] uranium, and iron.[4] Invert sugar is about seven times as effective as cane sugar in holding up hydrous ferric oxide. Grimaux[5] showed that glycerine prevents the precipitation of hydrous ferric oxide by caustic potash.

If one ion of an electrolyte is adsorbed more than the other ion, it will tend to peptize the adsorbing material and to give rise to a colloidal solution containing positively or negatively charged particles according to the nature of the adsorbed ion. Freshly precipitated silver halides are peptized by dilute silver nitrate or the corresponding potassium halide,[6] the silver and the halide ions being adsorbed strongly. Many oxides are peptized by their chlorides or nitrates, forming so-called basic salts.[7] Sulphides are peptized by hydrogen sulphide.[8] Gelatine is liquefied or peptized by a potassium iodide solution. The peptization of hydrous oxides by caustic alkali can be considered as a case of common ion or as the preferential adsorption of hydroxyl ion. Hydrous chromic oxide gives an apparently clear green solution when treated with an excess of caustic potash; but the green oxide can be filtered out completely by means of a collodion

[1] Weisberg: Bull. Soc. chim., Paris, (3) **15,** 1097 (1896).

[2] Lobry de Bruyn: Ber. deutsch. chem. Ges., **35,** 3079 (1902).

[3] Graham: Jour. Chem. Soc., **15,** 253 (1862).

[4] Riffard: Comptes rendus, **77,** 1103 (1873).

[5] Comptes rendus, **98,** 1485, 1540 (1884).

[6] Lottermoser: Jour. prakt. Chem. (2) **60,** 341 (1903); **72,** 39 (1905); **73,** 374 (1906); Zeit. phys. Chem., **62,** 371 (1908).

[7] Graham: Jour. Chem. Soc., **15,** 254 (1862); Müller: Ber. deutsch. chem. Ges., **39,** 2856 (1906); Zeit. anorg. Chem., **52,** 316 (1907); Szilard: Jour. Chim. phys., **5,** 488, 636 (1907).

[8] Spring: Ber. deutsch. chem. Ges., **16,** 1142 (1883); Prost: Jour. Chem. Soc., **54,** 653 (1888); Winssinger: Bull. Soc. chim., Paris (3) **49,** 452 (1888); Linder and Picton: Jour. Chem. Soc., **61,** 116 (1892); Meunier: Comptes rendus, **124,** 1151 (1897); Young: Jour. Phys. Chem., **21,** 141 (1917).

filter, a colorless solution passing through.[1] Hantzsch[2] considers that hydrous beryllium oxide is peptized by caustic alkali[3] and so is cobalt oxide.[4] In ammoniacal copper solutions part of the copper oxide it apparently colloidal and part dissolved.[5] Freshly precipitated zinc hydroxide is peptized by alkali; but the solution is very unstable, the zinc hydroxide often coagulating inside half an hour. The relatively small amount of zinc remaining in solution is present chiefly or entirely as sodium zincate.[6] The bulk of the evidence seems to be that alumina is not peptized appreciably by alkali and that it goes into solution as sodium aluminate,[7] though the other view has been supported.[8] Adsorption of hydroxyl ion accounts for the peptization of silicic acid[9] and of caseine by alkalies. Caseine can also be peptized by acids. A. Müller[10] has prepared colloidal solutions of aluminum, iron, cobalt, thorium, and yttrium oxides by peptization with dilute hydrochloric acid, and Bentley and Rose[11] have peptized freshly precipitated alumina with 8 percent acetic acid. It is possible but not probable, that the peptization is done by a trace of metallic salt formed by the acid and not by the hydrogen ion.

There are no cases where it has been shown conclusively that

[1] Fischer and Herz: Zeit. anorg. Chem., **31,** 352 (1902); Fischer: Ibid., **40,** 39 (1904); Nagel: Jour. Phys. Chem., **19,** 331, 569 (1915).

[2] Zeit. anorg. Chem., **30,** 289 (1902).

[3] Loew: Zeit. anal. Chem., **8,** 463 (1870); Fischer: Zeit. anorg. Chem., **40,** 39 (1904).

[4] Tubandt: Zeit. anorg. Chem., **45,** 368 (1905).

[5] Péligot: Ann. Chim. Phys. (3) **63,** 343 (1861); Guignet: Comptes rendus, **55,** 741 (1862); Grimaux: Ibid., **89,** 1434 (1884).

[6] Hantzsch: Zeit. anorg. Chem., **30,** 289 (1902); **75,** 371 (1912); Fischer and Herz: Zeit. anorg. Chem., **31,** 352 (1902); Klein: Zeit. anorg. Chem. **74,** 157 (1912).

[7] Herz: Zeit. anorg. Chem., **25,** 155 (1900); Hantzsch: Zeit. anorg. Chem., **30,** 289 (1902); Rubenbauer: Zeit. anorg. Chem., **30,** 331 (1902); Slade: Jour. Chem. Soc., **93,** 421 (1908); Zeit. anorg. Chem., **77,** 457 (1912); Trans. Faraday Soc., **10,** 150 (1914); Blum: Jour. Am. Chem. Soc., **35,** 1499 (1913).

[8] Mahin, Ingraham and Stewart: Jour. Am. Chem. Soc., **35,** 30 (1913).

[9] Graham: Jour. Chem. Soc., **17,** 324 (1864).

[10] Svedberg: Die Methoden zur Herstellung kolloider Lösungen anorganischer Stoffe, 400 (1909).

[11] Jour. Am. Chem. Soc., **35,** 1490 (1913).

peptization is due chiefly to adsorption of undissociated salt,[1] but undoubtedly such instances will be found. Water-peptizable colloids like gelatine,[2] gum arabic,[3] dextrine,[4] soap,[5] or saponin[6] will peptize many precipitates and they are often called protecting colloids because they prevent the agglomeration and consequent settling of finely divided precipitates. Caseine is not peptized by water; but acts as a protecting colloid when peptized by acids or alkalies. Hydrous chromic oxide when peptized by caustic potash, can then prevent the precipitation of hydrous ferric oxide, etc. If too much ferric oxide is present, all the chromic oxide is carried down by it.[7] Solutions of copper oxide in ammonia will peptize chromic oxide.[8] Molybdic acid is not precipitated from its salts by uranyl salts, but tungstic acid is. In presence of tungstic acid, practically all the molybdic acid is precipitated. This is obviously a case of adsorption and the converse is also true that no tungstic acid would be precipitated in presence of a sufficient excess of a molybdate.[9] Aniline dyes, which are insoluble in benzene can be peptized by a benzene-soluble colloid such as the so-called zinc or magnesium resinate.[10]

Since a colloidal solution is one in which a finely divided phase is kept from coalescing in some way, it is clear that there may be any number of colloidal aluminas, for instance, varying from anhydrous alumina (Al_2O_3) up to the most highly hydrous form that can be obtained. As a matter of fact, people have generally been satisfied with distinguishing only two sets of colloidal solutions, which they have called solutions of alumina and metal-

[1] It seems probable that the peptization of caseine by acetic acid is due largely to the undissociated acid.

[2] Eder's Handbuch der Photographie, 5th Ed., **3** I, 28 (1902); Lüppo-Cramer: Phot. Correspondenz, **44,** 578 (1907).

[3] Lefort and Thibault: Jour. Chem. Soc., **42,** 1322 (1882).

[4] Lachaud: Bull. Soc. chim., Paris (3) **15,** 1105 (1896).

[5] Spring: Zeit. Kolloidchemie, **4,** 161 (1909); **6,** 11, 109, 164 (1910).

[6] Schiaparelli: Jour. Chem. Soc., **46,** 333 (1884).

[7] Northcote and Church: Jour. Chem. Soc., **6,** 54 (1854); Nagel: Jour. Phys. Chem., **19,** 331 (1915).

[8] Prudhomme: Jour. Chem. Soc., **25,** 672 (1872).

[9] Miss Hitchcock: Jour. Am. Chem. Soc., **17,** 483, 520 (1895); Wöhler: Zeit. Elektrochemie, **16,** 693 (1910); Wöhler and Engels: Kolloidchemische Beihefte, **1,** 454 (1910).

[10] Soxhlet: Art of Dyeing and Staining Marble, etc., 76 (1902).

lumina, of stannic and metastannic acids, etc.[1] While adsorption will cause peptization under suitable conditions, the disintegrating power of the adsorbed substance is relatively small and often will not be sufficient to break up solid masses. A protecting colloid, for instance, will prevent the formation of a precipitate when it may not be able to disintegrate a massive precipitate.

[1] HANTZSCH: Zeit. anorg. Chem., **30,** 338 (1902).

CHAPTER VI

PREPARATION OF COLLOIDAL SOLUTIONS

The methods of making colloidal solutions can be grouped under two heads, the condensation methods and the dispersion methods. The condensation methods will be considered first.

Condensation Methods

In condensation methods we must have strong adsorption (including protecting colloids), or we must keep down the concentration of agglomerating agents either by choice of reagents or by dilution. A few instances will be given of the preparation of colloidal solutions in the presence of a strongly adsorbed substance. Colloidal palladium may be obtained by reduction with hydrazine in presence of gum arabic.[1] Colloidal solutions of silver chloride, silver bromide, or Prussian blue may be obtained by precipitation in presence of gelatine.[2] Sulphide solutions may be stabilized by gum arabic[3] or by sodium sulphide, but not by ammonium sulphide.[4] Silver chromate, hydrous copper oxide,[5] and hydrous ferric oxide may be obtained colloidal in presence of sugar.[6] Invert sugar holds up about seven times as much iron as cane sugar. Glycerol also enables us to make a colloidal solution of ferric oxide.[7] Gengou[8] prepared colloidal alumina and barium sulphate in presence of sodium citrate, and Schiaparelli[9] held up lead sulphide with saponin. A solution

[1] Svedberg: Die Methoden zur Herstellung kolloider Lösungen anorganischer Stoffe, 105 (1909).

[2] Svedberg, 323.

[3] Lefort and Thibault: Jour. Chem. Soc., **42,** 1322 (1882).

[4] Haussmann: Zeit. anorg. Chem., **40,** 121 (1904).

[5] Svedberg, 224, 304.

[6] Riffard: Jour. Chem. Soc., **27,** 292 (1874).

[7] Grimaux: Jour. Chem. Soc., **46,** 96 (1884).

[8] Zeit. Kolloidchemie, **9,** 88 (1911).

[9] Jour. Chem. Soc., **46,** 332 (1884).

obtained by adding sulphuric acid to barium arabinate was milky after standing four years.[1] Cadmium sulphide can be obtained colloidal in presence of caseine,[2] and so can copper oxide,[3] while mercurous chloride can be held up by albumin.[4] All the metals and many other substances can be kept in colloidal solution by sodium protalbinate and lysalbinate, which are salts of somewhat hypothetical acids obtained by saponification of albumin.[5] It is an open question whether they are any more effective than gelatine. Colloidal solutions of silver in organic solvents can be obtained with wool-fat as protecting colloid.[6] Carey Lea prepared colloidal silver of various colors by reduction of a silver salt with ferrous citrate or tartrate.[7] Both red and blue copper solutions have been obtained in presence of lysalbinates.[8] Colloidal gold and silver can be kept from coagulating by means of starch.[9] Mercury and bismuth may be kept up by stannic oxide[10] and gold by ceria,[11] while sodium sulphate keeps up sulphur in strongly acid solution and potassium sulphate precipitates it.[12] Acheson aquadag is kept in colloidal solution by tannin and iron oxide.[13]

In a number of other cases the concentration of the agglomerating agent is kept low either by selection of the reaction or by dilution. Since electrolytes are very effective in producing precipitation in many cases, this usually means keeping the concentration of electrolytes very low. It may make matters clearer to classify the methods according to the type of reaction involved.

1. Reduction without Electrolysis.—At 50° hydrogen gas reacts slowly with silver oxide in presence of water, the dissolved

[1] Jour. Chem. Soc., **30,** 538 (1876).

[2] Svedberg, 325.

[3] Rittenhausen: Jour. prakt. Chem. (2) **5,** 215 (1873); **7,** 361 (1874).

[4] Svedberg, 325.

[5] Svedberg, 125, 295, 327.

[6] Amberger: Zeit. Kolloidchemie, **11,** 99 (1912).

[7] Svedberg, 211.

[8] Svedberg, 166, 170.

[9] Gutbier and Weingärtner: Kolloidchemische Beihefte, **5,** 211, 244 (1913).

[10] Svedberg, 204.

[11] Schottländer: Jour. Chem. Soc., **68** II, 218 (1895).

[12] Svedberg, 249; Cf. Odén: Zeit. Kolloidchemie, **8,** 186 (1911).

[13] Cf. Doyle: Jour. Phys. Chem., **17,** 390 (1913).

silver oxide being the substance which reacts. The reaction is $Ag_2O + H_2 = 2Ag + H_2O$, so the silver is formed in the absence of electrolytes and tends to come down colloidal, though some does precipitate as a mirror.[1] From dilute solutions of gold salts, colloidal gold can be obtained by reduction with carbon monoxide, sulphur dioxide, formaldehyde, pinene, alcohol, hydrazine, and phenyl hydrazine.[2] In these cases the concentration of electrolytes is kept low by dilution. On the other hand, colloidal copper can be obtained by the action of alcohol on anhydrous copper sulphate and concentrated sulphuric acid,[3] a reaction which cannot be classified without further study. Colloidal gold can also be obtained by reduction by means of *Aspergillus oryzae*.[4] The effect of concentration has been studied by Liversidge.[5] Colloidal metals may also be obtained by reduction in flames.[6]

2. Reduction with Electrolysis.—When very dilute solutions of gold, silver, and mercury salts are electrolyzed, some of the metal comes out in colloidal form.[7] Billitzer[8] obtained colloidal solutions in a similar way with salts of the less noble metals, but it is probable that the dispersed phase consisted of oxide and not of metal.[9] Lecoq[10] has prepared colloidal arsenic electrolytically, and Sansonoff[11] colloidal UO_2, the latter being stabilized by uranyl chloride.

3. Oxidation.—Colloidal sulphur can be obtained from the reaction[12] between H_2S and SO_2, which involves no high concentration of electrolyte. In presence of gelatine as stabilizer, colloidal sulphur[13] can be obtained by oxidation of H_2S. Wöhler and Witzmann[14] have prepared iridium dioxide as a violet or

[1] Svedberg, 38.
[2] Svedberg, 60–71, 101, 112.
[3] Rasenfosse: Jour. Soc. Chem. Ind., **30,** 133 (1911).
[4] Svedberg, 199.
[5] Jour. Chem. Soc., **60,** 401 (1891).
[6] Donau: Zeit. Kolloidchemie, **16,** 81 (1915).
[7] Svedberg, 206.
[8] Ber. deutsch. chem. Ges., **35,** 1929 (1902).
[9] Haber: Zeit. Elektrochemie, **8,** 551 (1902).
[10] Comptes rendus, **150,** 700 (1910).
[11] Zeit. Kolloidchemie, **8,** 96 (1911).
[12] Svedberg, 243.
[13] Himmelbaur: Zeit. Kolloidchemie, **4,** 307 (1909).
[14] Zeit. anorg. Chem., **57,** 328 (1908).

blue solution. Bredig and Marek[1] have obtained colloidal manganese dioxide by the action of hydrogen peroxide on permanganate. When aurous chloride breaks down into a ric chloride and gold, the latter can be obtained colloidal under suitable conditions.[2]

4. Hydrolysis.—Water will hydrolyze any salt until the product of concentrations of the hydroxyl and hydrogen ions reaches a value of about 10^{-14}. If either base or acid is very sparingly soluble, the hydrolysis will run farther than if both are strong electrolytes. Equilibrium will be reached more rapidly if the solution is heated. If a dilute solution of ferric chloride is boiled for a few minutes and then cooled, it will not be blackened by hydrogen sulphide[3] and it will not form Prussian blue with potassium ferrocyanide.[4] On the other hand, addition of sodium sulphate or of sulphuric acid will cause a precipitation of hydrous ferric oxide. Colloidal solutions of the hydrous oxide can be obtained by hydrolysis of the acetates, the nitrates, or the chlorides, but not in general by the hydrolysis of sulphates, because sulphuric acid precipitates the colloidal solutions more readily than hydrochloric, nitric, or acetic acid. The so-called chromsulphuric acids are apparently special cases of colloidal solutions due to hydrolysis in sulphate solutions.[5] Colloidal solutions can also be obtained by hydrolysis of a few compounds which are not electrolytes,[6] such as silicon sulphide, ferric ethylate, and copper succinimide.

5. Metathetical Reactions.—When hydrogen sulphide acts on arsenious oxide, arsenious sulphide is formed practically in the absence of electrolytes, $As_2O_3 + 3H_2S = As_2S_3 + 3H_2O$. This colloidal solution can be made of the very high concentration of 3 grams As_2S_3 per 5 grams water.[7] The reaction between mercuric cyanide and hydrogen sulphide gives prussic acid in solution; but this is a very weak acid and has but slight

[1] Van Bemmelen Gedenkboek, 342 (1910).

[2] Vanino and Roessler: Zeit. Kolloidchemie, **6**, 289 (1910).

[3] Wright: Jour. Chem. Soc., **43**, 156 (1883).

[4] Svedberg, 260.

[5] Denham: Zeit. anorg. Chem., **57**, 378 (1908); Strong: Comptes rendus, **150**, 1172 (1910).

[6] Svedberg, 276.

[7] Svedberg, 297.

precipitating power.[1] Colloidal sulphides can also be obtained with salts of strong acids by working in sufficiently dilute solutions.[2] In some cases sodium chloride has relatively little precipitating power, and it is therefore possible to prepare colloidal solutions of silicic acid from sodium silicate, of the so-called stannic and metastannic acids from stannic chloride and sodium stannate respectively;[3] and of tungstic acid from sodium tungstate. The tungstic acid solution can be concentrated until it contains 80 percent tungstic acid and has a density of over 3.2, so that glass will float in it.[4]

If M/20 $AgNO_3$ is mixed with M/20 KCl, KBr, or KI, so that there is a slight excess of one or the other solution,[5] more or less of the silver halide stays in suspension, being charged positively in the one case owing to adsorption of silver ion, and charged negatively in the other case owing to adsorption of halide ion. A salt which is readily soluble in water can be obtained in a colloidal state by working in a solvent in which the salt is practically insoluble and therefore precipitates in an extremely finely divided state.[6] Thus colloidal sodium chloride can be obtained by the interaction of sodium malonic ester and chloracetic ester in ligroin.[7]

6. Decomposition by Light.—Colloidal solutions can be obtained when substances are precipitated by the action of light. Svedberg[8] has studied the action of light on gold solutions, and Wigand[9] the behavior of sulphur solutions. There are also several other interesting papers along similar lines.[10]

[1] Svedberg, 302.

[2] Winssinger: Jour. Chem. Soc., **54,** 911 (1888).

[3] Svedberg, 303.

[4] Müllfr: Van Bemmelen Gedenkboek, 416 (1910).

[5] Lottermoser: Jour. prakt. Chem. (2) **68,** 341 (1903); **72,** 39 (1905); **73,** 374 (1906); cf. Drucker: Zeit. Kolloidchemie, **4,** 216 (1910).

[6] Böttger: Jour. Chem. Soc., **36,** 107 (1878); von Weimarn: Zeit. Kolloidchemie, **7,** 92 (1910); **8,** 216 (1911); **11,** 651 (1912); cf. Pieroni: Gazz. chim. ital., **43** I, 197; Paternò and Megigrecianu, Ibid., 43 I, 439 (1913).

[7] Svedberg, 349.

[8] Zeit. Kolloidchemie, **6,** 238 (1910).

[9] Zeit. phys. Chem., **77,** 423 (1911).

[10] Amann: Zeit. Kolloidchemie, **8,** 197 (1911); Galecki: Ibid., **10,** 149 (1912); Hartwagner: Ibid., **16,** 70 (1915).

Dispersion Methods

Five different types of preparation of colloidal solutions by peptization may be distinguished:

1. Removal of Agglomerating Agent.—If a precipitate has settled from a colloidal solution owing to the addition of too much of an agglomerating agent, the precipitate may go back into apparent solution if the excess of agglomerating agent is washed out. No colloidal solution will be obtained if it is impossible to wash out the coagulating agent or if the agglomeration has gone too far.[1] If a silver halide precipitate is washed on a filter at once, the silver salt is apt to run through the filter when the excess of potassium salt has been removed and there is present only the amount which would have kept the silver halide in suspension originally. When the rare earth nitrates are precipitated by ammonia and then washed, they are liable to stay suspended in the liquid when the ammonium nitrate is nearly all removed. In alloy work stannic oxide should be washed with dilute nitric acid and not with water. Zinc sulphide is apt to form a colloidal solution when the ammonium salt is washed out,[2] and copper ferrocyanide does the same thing if all the copper sulphate is removed by washing.[3] In fact, Chatard[4] claims that the quickest way to wash a gelatinous precipitate is to evaporate the solution to dryness and heat before trying to wash. Merely evaporating on a water-bath is not always sufficient.[5]

2. Addition of Peptizing Agent.—Instead of washing out a precipitating agent, a peptizing agent may be added. Ammonia is very effective in suspending clay,[6] silicic acid is peptized readily by caustic soda,[7] and Prussian blue is peptized by oxalic acid or by potassium oxalate. In some cases the concentration of the peptizing agent has to be high, as when oxides are to be peptized by alkali, and people usually assume the formation of compounds.

[1] Cf. Abegg and von Schroeder: Zeit. Kolloidchemie, **2,** 85 (1907).

[2] Donnini: Jour. Chem. Soc., **66** II, 318 (1894).

[3] Berkeley and Hartley: Phil. Trans., **206A,** 486 (1906).

[4] Jour. Chem. Soc., **26,** 527 (1873).

[5] Wright: Jour. Chem., **43,** 156 (1883); Kratz: Jour. Phys. Chem., **16,** 121 (1912).

[6] Skey: Chem. News, **17,** 164 (1868); **22,** 236 (1870); **34,** 142 (1876). See also Doelter: Handbuch der Mineralchemie, **2,** 122 (1912).

[7] Graham: Jour. Chem. Soc., **17,** 324 (1864).

Jowitschitsch[1] describes conditions under which chromic oxide is apparently completely soluble in ammonia. This is probably a case of peptization.

The action of soap on rouge or carbon black[2] looks like a disintegration; but it is not. If a suspension of carbon black in water be filtered several times through filter-paper, the water will finally run through clear, and the carbon black will be held back by the filter-paper. If a soap solution be poured on the filter, a black filtrate is obtained and the filter-paper is no longer black. All the carbon black has passed through the filter-paper. The same thing can be done with rouge, except that a red filtrate is obtained instead of a black one. At first sight it seems as though the soap must have broken up the carbon or the rouge into finer particles, which then passed through the filter, but this is probably not so. The filter-paper is porous enough at first to let through the particles of carbon or rouge, as is shown by the fact that some of the suspended matter does pass through the filter at first. The cellulose adsorbs the carbon black or the rouge, and and this clogs the filter to such an extent that the pores are not large enough to let the remaining particles through. The soap removes the rouge or the carbon black from the paper because it adsorbs these substances more strongly, and everything, therefore, goes through the paper. That this is the true explanation can be shown in two ways. In the first place, the experiment does not succeed if the rouge or the carbon is too coarse. In the second place, Spring showed that we are dealing with an adsorption of carbon black by filter-paper. If the black filter-paper be reversed and washed with water, the water removes only the black which is not in immediate contact with the paper.

3. Mechanical Disintegration.—If a solid be ground up sufficiently fine, it will necessarily form a colloidal solution for a time. This has been done experimentally by Wegelin[3] in the case of a number of metals. The addition of gelatine makes it easier to disintegrate ductile metals.[4] It must be remembered that a

[1] Monatsheft für Chemie, **34,** 225 (1913).

[2] Spring: Zeit. Kolloidchemie, **4,** 161 (1909); **6,** 11, 109, 164 (1909).

[3] Zeit. Kolloidchemie, **14,** 65 (1914).

[4] Metallic inks are said to be made by grinding with honey. Thorpe: Dictionary of Applied Chemistry, **3,** 138 (1918).

powder made with gelatine will not necessarily have exactly the same properties as the same powder when pure. Tyndall[1] has called attention to one classical instance of an error due to overlooking the effect which a little gum might have on the adsorption of dark heat rays. Melloni found the same radiant and absorbent power for chalk and lamp-black. Masson and Courtépée studied a number of chemical precipitates and found that all manifested the same power of radiation. The conclusion was drawn that the influence of the fine state of division is so powerful as entirely to mask and over-ride whatever influence might be due to chemical constitution. As a matter of fact, the precipitates were mixed with a solution of gum in water and were then painted on the side of a cube with a brush. The gum coating is very transparent to light but as opaque as pitch or lamp-black to the longer non-luminous rays. The measurements all referred to a surface of gum and consequently all came out alike.

Since a finely divided solid is more soluble, it is possible that it may go into solution and then precipitate in another form. This seems to happen with quartz. When reduced to an impalpable powder by long grinding, quartz can be converted into colloidal hydrous silicic acid merely by boiling with water.[2]

4. Electrical Disintegration.—When a direct current arc is formed under water between two wires, the metal is disintegrated and colloidal solutions of platinum, iridium, palladium, gold, silver, and cadmium may be obtained in this way.[3] Satisfactory conditions are obtained with 30 to 40 volts and 5 to 10 amperes. A trace of alkali in the water causes formation of finer particles, presumably owing to the stabilizing effect of the hydroxyl ion. The disintegration is chiefly at the cathode.

The method is not satisfactory with organic liquids, because too much decomposition of the liquids takes place. Svedberg found empirically that this decomposition could be decreased very much if the current density were made as small as possible.[4]

[1] Fragments of Science: Radiant Heat and its Relations.

[2] Desch: The Chemistry and Testing of Cement, 58 (1911).

[3] Bredig: Zeit. Elektrochemie, **4**, 514 (1898); Zeit. phys. Chem., **31**, 258 (1899).

[4] Svedberg, 424.

He therefore used an oscillatory discharge from an induction coil with a condenser in parallel or in series. The best results are obtained with large capacity, small self-induction, low resistance, and short arc.[1] By this improved method Svedberg succeeded in preparing colloidal solutions of all the metals, including the alkali metals. Liquid methane, ether, and isobutyl alcohol at low temperature were especially satisfactory with the metals of the alkalies and the alkaline earths. The order of disintegration of some of the metals under similar conditions was found to be Fe, Cu, Ag, Al, Ca, Pt, Au, Zn, Sn, Cd, Sb, Tl, Bi, Pb, the iron being the least rapidly disintegrated and the lead the most rapidly. There is no apparent relation either with the order of the boiling-points or with the order of disintegration by cathode rays or canal rays.

5. Electrochemical Disintegration.—With a lead cathode in caustic soda solution, the lead disintegrates when the current density exceeds a critical value, and the solution is colored black like ink with fine particles of metallic lead.[2] This is due to the temporary formation of a sodium-lead alloy, which then disintegrates in contact with water. Similar results can be obtained with cathodes of tin, bismuth, thallium, arsenic, antimony, and mercury. E. Müller[3] obtained colloidal solutions of tellurium with a tellurium cathode. This seems to be due to the formation of polytellurides, which break down and set free tellurium. In the presence of oxygen there may be also an oxidation of a telluride. Fischer[4] has obtained metallic copper in the solution by using a high current density with a copper anode in sulphuric acid. Cuprous sulphate is formed, which breaks down to metallic copper and cupric sulphate. This experiment has not yet been made to give colloidal copper, but this could probably be done if one were to add a suitable protecting colloid.

[1] See also Morris-Airey and Long: Jour. Chem. Soc., **104** II, 1033 (1913); Long: Zeit. Kolloidchemie, **14,** 136 (1914); Kutscheroff: Ibid., **11,** 165 (1912); Zawrieff: Zeit. phys. Chem., **87,** 506 (1914).

[2] Reed: Jour. Franklin Inst., **139,** 283 (1895); Bredig and Haber: Ber. deutsch. chem. Ges., **31,** 2741 (1898); Haber and Sack: Zeit. Elektrochemie, **8,** 243 (1902); Zeit anorg. Chem., **34,** 286 (1903).

[3] Zeit. Elektrochemie, **11,** 521, 701 (1905); Haber: Ibid., **11,** 660, 827 (1905).

[4] Ibid., **9,** 507 (1903).

The disintegration of all electrodes by an alternating current when the current density is high is undoubtedly due to the temporary formation and subsequent breaking down of a hydrogen or metallic alloy.[1]

[1] HABER: Trans. Am. Electrochem. Soc., **2,** 192 (1902); VAN NAME: Zeit. Elektrochemie, **10,** 303 (1904).

CHAPTER VII

PROPERTIES OF COLLOIDAL SOLUTIONS

General Properties

The whole theory of colloidal solutions is based on the assumption that we are dealing with two-phase systems. Since this is not obvious and is still disputed by some people, it is important to see what independent proof we have of the existence of a second phase. If a beam of light strikes small particles in suspension in a transparent medium, the light is scattered and polarized, provided the refractive index of the particles differs from that of the transparent medium. The intensity of the scattered light is inversely proportional to the fourth power of the wavelength and the scattering by each particle is proportional to the square of the volume of the particle.[1] The scattered light is therefore chiefly blue.[2] This is known as the Tyndall phenomenon and it was used by him to determine whether air was free from dust and was optically empty. The same principle has been perfected and applied in the ultra-microscope,[3] so-called. In this instrument a powerful beam of light is focussed on the liquid to be examined and is looked at from the side through a powerful microscope.[4] If there are suspended particles in the liquid, they appear as bright points. One does not see the particles themselves but merely the light diffracted by them. With colloidal gold in glass it is possible to see that we have a two-phase system. By means of some form of this instrument there is no difficulty in demonstrating the existence of a second phase in many colloidal solutions. In fact the instrument is so delicate that one must guard against the danger of casual im-

[1] Rayleigh: Phil. Mag. (4), **41**, 107, 447 (1871).

[2] Instead of calling this by the clumsy term of the blue of turbid media, it would be very appropriate to speak of Tyndall blue.

[3] Siedentopf and Zsigmondy: Drude's Ann., **10**, 1 (1903).

[4] For a general discussion of the ultra-microscope, see Burton: The Physical Properties of Colloidal Solutions, 28 (1916).

purities making one see a second phase when it is not there. This difficulty becomes very serious with liquids other than water.

The recent work of Martin[1] seems to prove that some organic liquids scatter light even when absolutely pure. In so far as this may be true for a pure liquid or a true solution, the evidence of the ultra-microscope is not conclusive as to heterogeneity.

Although the particles themselves are not seen, it is possible to estimate their size if one knows the number and mass, and assumes that the particles are practically spherical. It is customary to use the word "microns" for particles with diameters exceeding 250$\mu\mu$, while those particles ranging from 6–250$\mu\mu$ are called submicrons, and the term amicrons is used for particles with a diameter less than 6$\mu\mu$. The existence of these smallest particles can be shown in certain cases because the particles may serve as nuclei for crystallization. Kogonossoff[2] claims to have followed the electrolysis of silver nitrate solutions with the ultra-microscope. Since the visibility of particles depends on the difference in index of refraction of the particles and the medium, it is evident that the more hydrous the second phase, the less easily can it be seen. With many organic colloids the particles can be seen only when they exceed 40$\mu\mu$ in diameter. The Brownian movements are consequently much less marked.

It is possible to prepare salt solutions which are optically empty. On the other hand Lobry de Bruyn[3] claims to have found that cane sugar solutions were optically inhomogeneous. This has been cited as a case of a large molecule being visible; but it is much more likely that the scattering was due to an impurity and not to the sugar itself. It apparently seems obvious to most people that if one continues to subdivide a precipitate sufficiently, one will pass from a suspension to a true solution without a break.[4] The fallacy lies in the assumption that one can have all sizes of particles in equilibrium with the liquid. Since the solid becomes more soluble the more finely subdivided it is, there will be particles of a certain size which will dissolve

[1] Jour. Phys. Chem., **24,** 478 (1920).

[2] Zeit. Kolloidchemie, **7,** 129 (1910).

[3] Rev. Trav. chim. Pays-Bas, **23,** 218 (1904).

[4] See, however, VON WEIMARN: Zur Lehre von den Zuständen der Materie, 161 (1914).

and reprecipitate in a coarser form and which therefore cannot coexist for any length of time with the liquid. This comes out clearly in the case of smokes, it being very difficult to obtain a stable smoke of satisfactory concentration with particles less than $10\mu\mu$. If one takes definite amounts of benzene and water, it is possible theoretically to subdivide the benzene so that it will dissolve completely in the water; but the true solution thus formed would have different properties from the corresponding suspension. It would show characteristic osmotic pressure phenomena and it would be instable in quite a different way from the suspension. While it is perfectly possible to treat a solution formally as the end term in a series of suspensions, there is nothing as yet to show that this is a desirable hypothesis.[1]

The presence of a second phase in a colloidal solution can also be shown by what is called ultra-filtration. A colloidal solution goes right through an ordinary filter; but Bechhold[2] showed that it was possible to form, on filter paper or wire gauze, collodion films with varying amounts of acetic acid or gelatine films hardened with formaldehyde, such that pores of almost any desired size can be obtained. By taking a filter with sufficiently fine pores, almost any colloidal solution can be filtered so as to leave the suspended matter behind. With a more porous filter the finer particles go through and the coarser ones are held back. In this way it is possible to get an approximate idea of the relative sizes of the particles in two different colloidal solutions. Solutions made up by Bechhold are arranged in Table XLII in the order of increasing fineness of particles. Blue colloidal solutions of litmus have finer particles in them than the corresponding red solutions.

Solutions made up in other ways would give different results, because colloidal gold solutions, for instance, can be made with particles of very different sizes. The deep green solution formed when chromic oxide is peptized by alkali comes through colorless when a suitable ultra-filter is used. On standing, the chromic oxide eventually becomes so coarse that it can be separated by means of an ordinary paper filter. In all cases of ultra-filtra-

[1] Cf. LeBlanc: Zeit. Elektrochemie, **19,** 794 (1913).

[2] Zeit. phys. Chem., **60,** 257 (1907); **64,** 328 (1908); Schoep: Zeit. Kolloidchemie, **8,** 80 (1911); Malfitano: Comptes rendus, **131,** 1229 (1904).

tion, care must be taken to ensure that a real filtration is taking place and that the results are not vitiated by adsorption. It is to be noted that the behavior of ultra-filters can be accounted for on the basis of size of pores and size of particles, which is not true for semi-permeable membranes.[1] On the other hand there seems to be some difficulty in determining the absolute size of the pores. Experiments by the bubble method with the ultra-filter indicated that the size of the colloidal silver (or collargol) particles was 200–490$\mu\mu$ whereas experiments with a Chamberland filter indicated that the coarsest collargol particles were less than 170$\mu\mu$ in diameter. In Table XLII they are called 20$\mu\mu$.

TABLE XLII.—ORDER OF ULTRAFILTRATION

Coarse suspensions	1 percent gelatine
Prussian blue	1 percent hemoglobin
Platinum sols (Bredig)	Serum albumin
Iron oxide	Diphtheria toxin
Caseine	Protalbumoses
Arsenious sulphide	Silicic acid
Gold (about 40$\mu\mu$)	Lysalbinic acid
Bismuth oxide	Deutero albumoses
Lysargin (silver)	Litmus
Collargol (silver, 20$\mu\mu$)	Dextrin
Gold	Crystalloids

With a suitable ultra-filter it is possible to filter ordinary water so that it is absolutely sterile. It is also possible to obtain in this way water which can be used for work with the ultra-microscope. The behavior of mixtures is distinctly interesting. If the two substances do not either one adsorb the other and if the particles are of different sizes, a separation can be effected. The green mixture of Prussian blue and hemoglobin filters red with a suitable filter, the fine hemoglobin going through and the coarse Prussian blue remaining behind. In a mixture of Prussian blue with arsenic sulphide or ferric oxide, there is adsorption and everything is stopped by a filter which would let through either the arsenic sulphide alone or the ferric oxide alone. By adding a protecting colloid, sodium lysalbinate, to Prussian blue further dispersion takes place and the Prussian blue will pass through a filter which just stopped it before. If serum albumin is added

[1] WALDEN: Zeit. phys. Chem., **10**, 699 (1892).

to Prussian blue and then oxalic acid, the Prussian blue particles are found to be smaller than before. If oxalic acid is added and then the serum albumin, no marked change in the size of particles takes place. Undoubtedly the oxalic acid is adsorbed by the Prussian blue and prevents the adsorption of the albumin to a considerable extent.

Since the existence of a colloidal solution depends on the Brownian movements counteracting the force of gravity, it follows that if we increase the force of gravity, a colloidal solution will become less stable and may precipitate. This can be realized experimentally by centrifuging.[1] The best known case of this is the separator in which the cream, being lighter, goes to the center while the milk is thrown to the outside. A few precipitations of other solutions have been made; but the subject has not been studied systematically. At 4000 revolutions per minute gold submicrons are precipitated in a few minutes while the fine amicrons of Fe_2O_3 are not precipitated. With a super-centrifuge running 40,000 revolutions per minute and more, it is possible to precipitate many more colloidal solutions. The converse is also true, that a solution becomes more stable against centrifuging if the particles are made smaller. A separator does not give cream with homogenized milk in which the fat particles are less than 0.8μ in diameter.[2] The fact that a true solution, if practically saturated, can be made to crystallize by centrifuging,[3] does not indicate any real analogy between true and colloidal solutions. In the case of the true solution, only a small amount of the dissolved substance can be precipitated while with a colloidal solution practically all the suspended material comes down.[4]

A coarse suspension, if entirely insoluble and anhydrous, should give rise to no osmotic pressure, no diffusion except as a result of electrical charges, and no change in surface tension or

[1] Franklin and Freudenberger: Trans. Am. Electrochem. Soc., **8,** 29 (1903); Giolitti: Gazz. chim. ital., **36** II, 159 (1906); Dumanski: Van Bemmelen Gedenkboek, 421; Friedenthal: Zeit. Kolloidchemie, **15,** 75 (1914); Ayres: Met. Chem. Eng., **14,** 500 (1916).

[2] Fleischmann: Lehrbuch der Milchwirtschaft, 393 (1906).

[3] Bredig: Zeit. phys. Chem., **17,** 459 (1895); Lobry de Bruyn and van Calcar: Rec. Trav. chim. Pays-Bas, **23,** 218 (1904).

[4] Bechhold: Zeit. Kolloidchemie, **2,** 3 (1907).

conductivity. If the suspension is hydrous it may have a marked effect on the surface tension. In fact Lottermoser[1] has suggested that the hydrous colloid may sometimes be the external phase. In general the apparent osmotic pressures of colloidal solutions are very small and this has led to absurd molecular weights.[2] Such values as 30,000 for albumin, 700,000 for glycogen, over 48,000 for silica and "enormous" for Fe_2O_3 mean nothing whatsoever. This can be seen readily if we consider the case of boiling water to which scrap platinum is added to prevent overheating. Nobody would deduce a molecular weight of platinum from such an experiment, not even if the platinum were sub-divided a good deal, and yet this is just what people do continually with colloids. If one adds water to benzene, a little will dissolve and will change the freezing point of the benzene. From this one can calculate the molecular weight of water dissolved in benzene; but the calculation means nothing so soon as there is an excess of water. It would still mean nothing if one were to break the water up into drops which stayed suspended for a while in the benzene.

It is not denied that colloidal solutions may show osmotic phenomena. This may happen in case the suspended material is somewhat soluble or contains adsorbed soluble material.[3] It is wrong, however, to refer the observed osmotic pressure to the total amount of added material. It is also wrong to study the swelling of jellies and to speak of the results as measurements of osmotic pressure.

The low rate of diffusion of colloids was the phenomenon which first started Graham on his studies in regard to colloids. There is no question but that colloids do diffuse. This may be due in part to adsorbed material, but we also get a diffusion due to the Brownian movements, since the bombardment by the molecules of the medium apparently tends to produce a uniform distribution of the suspended particles, except in so far as this is interfered with by gravity, surface tension, electrical stresses, etc.

[1] Van Bemmelen Gedenkboek, 152 (1910).

[2] Gladstone: Phil. Mag. (5) **2**, 838 (1889); Sabaneeff: Jour. Chem. Soc., **58**, 1215 (1890); Reid: Jour. Physiology, **31**, 438 (1904); Gatin-Gruzewska: Jour. Phys. Chem. **8**, 515 (1904); Euler: Pflanzenchemie, **2**, 33 (1908); Chwolson: Jour. Phys. Chem., **16**, 88 (1912).

[3] Bayliss: Proc. Roy. Soc., **81**, 269 (1909); Biltz and von Vegesack: Zeit. phys. Chem., **68**, 357 (1909).

The diffusion of a colloid through certain membranes is practically zero, while true solutions go through readily. This property has been made use of to purify colloidal material from dissolved substances. The process is called dialysis. In its simplest form a tube, closed at one end with a parchment paper or animal membrane, is filled with the solution to be dialyzed and is placed in a larger vessel filled with distilled water. The dissolved substances diffuse out and the colloidal material is left behind.

Wintgen[1] claims that the reciprocal of the density, the specific volume, is practically a linear function of the percentage concentration by weight. This was tested with arsenic sulphide, antimony sulphide, silicic acid, molybdic acid, ferric oxide, tannin, starch, gelatine, albumin, sodium caseinate so-called, and serum globulin. If extrapolation is made to 100 percent colloid the value for the specific volume comes out too low and consequently the value for the density too high. This is probably due to the existence of a film of condensed water around each particle. If the suspended matter be in practically stable equilibrium, the density as determined by the hydrometer will be the same as that determined by weighing a given volume.[2] If the suspended material is settling or rising with sufficient rapidity, the density shown by the hydrometer will be that of the liquid medium. It is all a question of the extent to which the immersion of the hydrometer displaces water or displaces water and suspended material. It is another form of the problem whether a beaker weighs more in case a fly, which is heavier than air, hovers in the beaker without touching it. So long as the fly is there, the fly and the air are equivalent to a medium which is denser than air and consequently the downward thrust is greater when the fly is there than when it is not. If anybody doubts this, let him consider the case where a glass plate is laid over the mouth of the beaker imprisoning the hovering fly.

The product of the specific volume into the index of refraction is said to be a linear function of the percentage composition by weight.[3]

[1] Kolloidchemische Beihefte, **7**, 251 (1915).

[2] Bondy: Pogg. Ann., **121**, 314 (1865); Owens: Geographical Journal, **37**, 68 (1911); Ehrenberg: Die Bodenkolloide, 84 (1915).

[3] Wintgen: Kolloidchemische Beihefte, **7**, 268 (1915).

An anhydrous substance in suspension, such as ferric oxide,[1] arsenic sulphide, gold, etc., appears to have no effect on the surface tension of the medium; but some of the gelatinous colloids have a marked effect. Soap lowers the surface tension a great deal. Addition of 0.5–0.8 g gelatine to 100 cc water causes a marked decrease in the surface tension of water, while addition of further amounts has practically no effect.[2] Addition of gum arabic increases the surface tension within the same limits. We do not know why this last should be so.

It has already been shown that when oleic acid is dropped on a water surface a portion is adsorbed and spreads over the surface, while the excess, if slight in amount, draws up into drops. The thickness of the adsorbed oil film will vary from nothing up to that where the drop formation occurs. If water peptized oleic acid appreciably, we should find that, for a given small amount of oil, the surface film would be thinner the greater the peptizing action of the liquid or the greater the surface relatively to the mass. Conversely, if we started with a peptized mass, some of the oil would go into the surface and form a film there. This has been studied in some detail by Metcalf,[3] who did not realize that he was dealing with colloidal solutions. He found that peptone solutions gradually formed an elastic surface film with properties depending on the temperature. As the rate of diffusion was very slow, this film could be prepared more readily by dropping a concentrated peptone solution on the surface of pure water. The difference in concentration between the surface and the mass of the liquid was too great to be accounted for by the Gibbs formula for the relation between change of surface tension and change of concentration in the surface film. Consequently Metcalf assumed the existence of an insoluble form of peptone. This cannot be the true explanation because the phenomenon is general. The difficulties disappear the moment one realizes that it is a question of colloidal solution and not of a balancing of osmotic pressures. Saponin[4] also forms a markedly

[1] Linder and Picton: Jour. Chem. Soc., **60,** 72 (1895); Zlobicki: Ibid., **87,** 1924 (1905).

[2] Zlobicki: Bull. Acad. Sci. Cracovie, **1906,** 497.

[3] Zeit. phys. Chem., **52,** 1 (1905).

[4] Shorter: Phil. Mag. (6) **11,** 317 (1906); **17,** 560 (1909).

viscous surface film. It is familiar to everybody that a skin forms readily over boiled milk or over cocoa. The more rapid formation after heating is undoubtedly due to the colloidal solution becoming less stable, though this has not been proved experimentally, nor has it yet been shown that the film is thinner the greater the peptizing action of the liquid.

Since the film formation will occur more readily and more rapidly if the colloidal substance adsorbs air to a marked extent and since air is always present in actual experiments, a further discussion of film formation from colloidal solution will be left till we take up emulsions and froths.

Viscosity

The viscosity of a liquid is the resistance offered to shearing, to stirring, or to the flow through a capillary tube.[1] The viscosity coefficient is the force required to move at unit velocity a plate of unit surface separated from another plate of the same size by a layer of liquid of unit thickness. In the case of water-soluble colloids the viscosity may increase enormously with the concentration, a 1 percent solution of agar forming a solid jelly. This is undoubtedly in part a question of structure just as we know it is when 99 percent of kerosene is emulsified in a 1 percent of a soap solution. Here we have minute globules of oil coated by viscous soap films which coalesce to form a honeycomb structure. The metal and the sulphide sols have only a very slight effect on the viscosity of water. This varies with the nature and the sub-division of the solid particles. According to Hatschek 20-30 percent of precipitated calcium carbonate or barium sulphate does not increase the viscosity very much. On the other hand, Bingham[2] found zero fluidity or infinite viscosity with 4 percent of china clay or 5.5 percent of graphite.

Einstein[3] has deduced[4] a formula for the viscosity (η_1) of a suspension of rigid spheres in any liquid, in terms of the viscosity

[1] Hatschek: An Introduction to the Physics and Chemistry of Colloids, 21 (1916).

[2] Am. Chem. Jour., **46**, 278 (1911); Jour. Franklin Inst., **181**, 845 (1916).

[3] Drude's Ann., **19**, 289 (1906).

[4] Burton: The Physical Properties of Colloidal Solutions, 162 (1916).

(η) of the pure liquid and the ratio (f) of the volume of the suspended matter to the total volume,

$$\eta_1 = \eta(1 + kf)$$

where k is a constant which Einstein at first considered equal to unity but which he afterwards made equal to 2.5. A similar formula has been deduced by Hatschek[1] for cases where the suspended material occupies less than 40 percent of the total volume. It differs from Einstein's formula by having $k = 4.5$. This formula was tested by Harrison[2] for starch and water and was found to hold fairly well up to 30 percent concentration. According to these formulas, the viscosity depends only on the volume of the dispersed phase and not at all upon the degree of dispersity. Odén[3] found, however, an approximately 50 percent greater viscosity with sulphur sols in which the particles had a diameter of about $10\mu\mu$ than with sols in which the sulphur particles had a diameter of about $100\mu\mu$. Hatschek[4] attributes this very properly to the existence of an adsorption film of liquid around the sulphur particles, a phenomenon which was not considered when the formula was deduced. On the assumption that the thickness of the adsorbed film is independent of the size of the particles, Hatschek deduces that the thickness is about $0.87\mu\mu$ which corresponds to an increase in volume of about 62 percent for particles having a diameter of $10\mu\mu$.

Hatschek[5] has also deduced a formula for the viscosity of two liquid phases in which the volume of the dispersed phase is the larger,

$$\eta_1 = \eta \frac{\sqrt[3]{A}}{\sqrt[3]{A} - 1}$$

where $A = 1/f$ and is the ratio of the total volume to the volume of the dispersed phase. From this formula he deduces that one volume of caseine binds more than eleven volumes of water and that in a 0.4 – 0.5 percent rubber sol, the rubber binds 75–100 volumes of liquid.

[1] Zeit. Kolloidchemie, **7,** 301 (1910).
[2] Jour. Soc. Dyers and Colorists, **27,** April (1911).
[3] Zeit. phys. Chem., **80,** 709 (1912).
[4] Zeit. Kolloidchemie, **11,** 280 (1912).
[5] Ibid., **8,** 34 (1911); **11,** 284 (1912); **12,** 238 (1913).

We get rather curious results if we apply Hatschek's views on viscosity to Bingham's experiments on zero fluidity. If we make the assumption that plastic flow is reached when the surfaces of adsorbed water are in contact and if we make the further assumption that we are dealing with spheres in open piling, the voids will then be 48 percent of the whole and, in the case of graphite for instance, the amount of water adsorbed by the graphite must be $94.5 - 48 = 47.5$ volume percent, or each volume of graphite must adsorb about nine volumes of water. If we assume close piling or different sizes of graphite powder, the voids will be less and the amount of water to be adsorbed will be greater. Since the volumes of two spheres are proportional to the cubes of the radii, one volume of graphite will hold seven volumes of water if the thickness of the water film is equal to the radius of the graphite particles. If the thickness of the water film is 1.2 times the radius, the graphite will hold eleven volumes of water. This is the same type of calculation that Hatschek made and it shows that it is theoretically possible on this assumption to account for zero fluidity in a graphite-water mixture containing 5.5 percent graphite. It has not been shown, however, that the adsorbed films of water on the graphite particles are of the desired thickness, nor has it been shown that 47 percent of the water in the mixture is in a different state from the rest of the water. It might be possible to do this last by measuring the vapor pressure curve for graphite-water mixtures.

If the suspended particles aggregate into chains, the viscosity will be increased very much. If the particles form larger spherical particles which are homogeneous, there will be a decrease in the viscosity, because of the decrease in the surface and consequently in the amount of bound water. If, however, the particles simply agglomerate loosely into spherical masses, the viscosity will increase because the water in the voids inside the spherical agglomerates no longer counts as free water. We shall therefore expect to get an increase of viscosity as a result of agglomeration when the effect of agglomeration is not to increase the size of homogeneous drops.

One very interesting case of the effect of viscosity and presumably of the adsorbed water film occurs in the settling of slimes or pulps. Here the particles vary in size from those

coarse enough to settle moderately rapidly down to those so fine that the Brownian movements tend to keep them up completely. If there is a large amount of water present and the pulps are consequently very dilute, each particle separates practically unaffected by the others. The upper part of the liquid remains cloudy owing to the presence of the very fine particles, there is no sharp line of demarcation in the liquid, and there is, or may be, a sharp line at the bottom separating the coarser particles which have settled and the supernatant liquid.[1] With increasing concentration the coarser particles tend to interfere with the finer ones and to carry them down. The suspended pulp seems to settle as a whole, the upper portion of the liquid is practically clear with a sharp line separating it from the settling mud, and there is no visible dividing line at the bottom of the vessel between the slimes which have settled and those which are settling. According to Free the change from one type to the other came at about 8–9 percent with the kaolin suspension that he took, the higher concentrations giving what he calls consolidation settling and the lower concentrations subsidence settling.

When a given volume of pulp settles, an equal volume of water must rise and when the pulp is fairly viscous, it acts practically as a filter, removing all the finest particles.[2] Deane says that the effect of reducing the resistance to the upward flow of the water by creating a channel for the passage of the liquid can be shown very well by placing a sample of pulp in two test-tubes, one of which is held vertically, while the other is inclined slightly. In addition to the increased clarification in the inclined tube due to the increased settling area, it will be noticed that the pulp in settling away from the upper surface of the tube leaves an open channel which facilitates the free passage of the liquid. The rising current of the liquid on the upward surface and the settling of the solid on the lower surface is quite marked. If wires are placed vertically in a tank and are given rapid vibrations of low amplitude, this will cause channelling and will hasten thickening by making the upward flow of the liquid easier.

The dairymen have noticed that, contrary to what one would

[1] Owens: Geographical Journal, **37,** 68 (1911); Free: Eng. Min. Jour., **109,** 601 (1916).

[2] Deane: Trans. Am. Electrochem. Soc., **37** (1920).

expect, cream rises more rapidly and more completely in a deep vessel than in a shallow pan.[1] The finer particles of butter fat are caught by the coarser ones and swept upwards because the concentration of the coarser particles per unit of cross-section soon becomes high enough to have a filtering effect. The difference between this and the ore pulp is that the cream rises and filters upwards, while the pulp settles and filters downwards. In neither case has anybody made any experiments as to any possible relation between the concentration at which the filtration becomes effective and the concentration for zero fluidity.

Arisz[2] has made a number of valuable experiments on the viscosity of gelatine peptized at 50°–60° by glycerine of 1.176 specific gravity, corresponding to about 32 percent of water in the glycerine. He finds that above 65° there is a continuous decrease in the viscosity of the gelatine sols. At 95° the viscosity of a 10 percent sol dropped in thirty minutes to 92 percent of the viscosity which it had three minutes after reaching 95°. At 85° the drop was only to 97 percent in thirty minutes and at 75° to 99 percent. At 65° there was no change in viscosity in twenty-four hours. Arisz believes, apparently properly, that the change above 65° is due to a progressive decomposition of the gelatine which becomes negligible at and below this temperature. At 65° equilibrium is reached in less than three minutes and at lower temperatures with ever-increasing slowness. For 10 percent gelatine in the standard glycerine, Arisz considers that the equilibrium values for the viscosity as determined in the Ostwald viscosimeter are: 222 at 65°; 415 at 55°; about 950 at 50°; less than 4200 at 47°; about 5000 at 46°; and more than 30,000 at 44°, which is about the temperature at which the sol sets to a jelly. Since equilibrium is reached slowly at the lower temperatures, the viscosity of the sol will be less than the equilibrium value if the sol is cooled say from 65° to 55° and the viscosity will increase with time. If a sol in equilibrium at say 46° is heated to 55°, the viscosity will be greater than the equilibrium value and will decrease with increasing time. Until equilibrium is reached, the viscosity of a given gelatine-glycerine sol will thus

[1] McKay and Larsen: Principles and Practice of Butter-making, 125 (1906).

[2] Kolloidchemische Beihefte, **7**, 1 (1915).

depend at temperatures below 65° on the previous history of the sample and on the time that it has been held at the temperature in question.

These gelatine sols show the Tyndall beam and Arisz finds that the intensity of the scattered light increases with falling temperature and with increasing time, provided the viscosity is below the equilibrium value. Cooling a 1 percent gelatine-glycerine sol from 70° to 20° caused a four-fold increase in the intensity of the scattered light. When a similar solution was cooled to 18° and held there, the intensity of the scattered light at the end of nine days was nearly six times the initial value at 18°. There is therefore a parallelism between the changes in the Tyndall effect and the changes in the viscosity of these sols, and consequently part at least of the viscosity changes must be due to an agglomeration of the particles. Arisz considers that the small drops or particles have run together to form larger drops; but this cannot be true because that would mean a decrease in the viscosity and not an increase. The increase in the apparent size of the particles which one must assume in order to account for the Tyndall effect can be due equally well to an agglomeration of particles or drops without having them coalesce to a homogeneous particle or drop. That this is what actually happens is made probable by the experiments of Meyer[1] on starch. This of course does not exclude the possibility of viscosity changes due to displacement of equilibrium between two forms of gelatine[2] in case these exist. The important point is that the increase in viscosity does go hand in hand with an increase in agglomeration which must mean that increasing agglomeration involves decrease in the amount of available free water. The phenomenon is apparently general because Freundlich[3] has made use of the increase in viscosity as a means of studying the rate of agglomeration of alumina sols.

With colloidal solutions of gelatine and other substances of the same type, the viscosity changes with the time, showing that there is a gradual change in structure. This is further confirmed by the fact that the viscosity of such solutions changes when they

[1] Kolloidchemische Beihefte, **5**, 1 (1913).
[2] Smith: Jour. Am. Chem. Soc., **41**, 135 (1919).
[3] Trans. Faraday Soc., **9**, 66 (1913).

are shaken violently. Until we know more than we do now about the physical state of these colloidal solutions, it is distinctly unwise to predict anything very definite about their viscosities.

Where a film formation is possible, the surface viscosity will be quite different from that in the mass of the liquid. This is very striking in the case of colloidal solutions of saponin, peptone, etc. With saponin the surface viscosity is 60 times that of the mass of the liquid.[1] With peptone the film is so solid that the surface viscosity cannot be measured.

Color

It will simplify matters not to limit the discussion to the colors of colloidal solutions, but to consider something about the colors of colloids in general. The colors which depend on physical structure and not on pigments are known as structural colors and are often connected with the presence of colloidal material. An absolutely smooth reflecting surface is invisible. It is only when the specular reflection is changed to some extent to diffuse reflection that we see the surface. It was suggested that the Zeppelins should be coated with a polished surface of metallic chromium so as to make them invisible. While it would be impossible to see such a surface, almost anybody would realize that something queer was going on if he should happen to see a reflected portion of the earth's surface apparently moving along in the sky. While this last might never happen, the reflection of light from the polished surface would more than counterbalance the advantages of the theoretical invisibility.

A substance is also invisible if there is no reflection or refraction at its surfaces. If we suspend a transparent powder in a transparent liquid having the same index of refraction, the powder will be invisible. Some glass powders in carbon bisulphide are practically invisible. If a glass rod is dipped into a mixture of olive oil and cassia oil, the rod appears only to reach to the surface of the liquid for it cannot be seen in the liquid.[2] It may happen, however, that the dispersion of the liquid mixture differs from that of the solid, in which case there will be an agreement of

[1] Malcolm: Phil. Mag. (6) **12,** 508 (1906).

[2] Von Bezold: Die Farbenlehre, 62 (1874).

refractive index only for certain wave-lengths, which will be transmitted. We may therefore get the transmission of colored light, a phenomenon first studied by Christiansen.[1] When clean powdered glass is immersed in carbon bisulphide and benzene is added, the transmitted light is first red, then yellow, green, and blue in succession. For the same mixture, the transmitted light changes towards the blue with rising temperature.[2] In some cases the light is extremely pure, the range of refrangibility being only two and a half times that included by the two D lines.[3]

If we have a thin film with light reflected from the front and the back surfaces, it may happen that the crest of certain waves reflected from one surface will coincide with the hollow of waves reflected from the other surface, in which case this particular color will disappear and the place where this disappearance occurs will appear to have the complementary color. The colors of thin films[4] are often known as Newton's Rings. We are quite familiar with them in the case of soap bubbles and with oil films on the ground. In the streets of Washington the colors of the oil films are exceptionally brilliant; but this is not due to any particular brand of oil which is spilled there. It is because the streets are asphalted and consequently there is practically no reflection of light from the asphalt surface to interfere with the colors of thin films. This is a very good illustration of the importance of a dark background in the case of structural colors. The colors of tempered steel, of lead skimmings, of Nobili's metallochromes, and the flashing colors of certain insects' wings are further illustrations of the colors of thin plates. If black ice is struck with a heavy stick, the colors of thin plates appear in great beauty at the fractured surfaces.

We may get colors by reflection and refraction. The rainbow is an illustration of this. The old-fashioned cut-glass chandelier gives a good example of the colors that may be produced by light passing through a prism. If we have a number of lines ruled parallel and very close together on a smooth surface, this gives us what is known as a diffraction grating, which may spread a ray

[1] Wied. Ann., **23,** 289 (1884).
[2] Wood: Physical Optics, 110 (1911).
[3] Rayleigh: Proc. Roy. Inst., **16,** 116 (1889).
[4] Tyndall: Electricity and Light, 97 (1895).

of light out in a way very similar to a prism. Agates are composed of thin films about 0.001 of a millimeter in thickness, and when the agate is properly cut it may behave like a diffraction grating.[1] In the case of mother-of-pearl, we have alternate layers of calcium carbonate and an organic material. These layers overlap very slightly in a regular fashion and consequently act to some extent like a diffraction grating, giving rise to the peculiar effect known as pearly lustre.[2]

The reflection of light by powdered material may give rise to a number of interesting color phenomena. When white light is scattered from a surface instead of being reflected as in a mirror, it gives rise to the sensation of white. A block of ice is not white, because it does not scatter the light. If the ice is powdered, or still better if we have snow, the light is scattered and we call the snow white. Instead of having solid particles of ice in air we may have air bubbles embedded in liquid, and then we get a white froth or foam. If the blue crystals of copper sulphate are ground to a fine powder, the light passes through such fine layers of the material that it does not become colored blue to any appreciable extent. On the other hand, the light is scattered from the powdered surfaces, and the powdered copper sulphate looks white instead of blue. When silver is precipitated by an electric current, it does not come down with a mirror-like surface, but rather in a mass of tiny crystals which scatter the light in every direction. Consequently electrolytic silver is white and only has the characteristic appearance of silver after it has been burnished. There is no white pigment in any white flowers, or in white hair, and probably not in white bark. The white color of the lily is due to the presence of innumerable air bubbles and the same is true of white hair. In order that hair may turn white in a single night, it is not necessary for the original pigment to disappear and for white pigment to develop. It is only necessary for a mass of minute air bubbles to be formed in the hair as a result of worry. While this accounts for the physical change, we are as much at a loss as ever to know why intense grief should develop air bubbles in the hair.

The scattering of light by a powder or by the fibers of a sheet

[1] Goodchild: Precious Stones, 165 (1908).

[2] Pfund: Jour. Franklin Inst. **183,** 453 (1917).

of paper is due to the difference in the index of refraction between the solid particles and the air. If we replace the air by some liquid having very nearly the same index of refraction as the solid particles, these latter will cease to be white and will become more transparent. It is well known that oiled paper is distinctly translucent. If powdered copper sulphate were immersed in a liquid having about the same index of refraction as the crystals, these would probably become blue. This experiment has not been tried; but there is a more interesting one which has puzzled people for a good while. In the zoological gardens some flamingoes are much redder than others. At one time it was thought that the redness was connected with a fish diet; but flamingoes have been raised which had bright red feathers even though the birds had never eaten fish, so this explanation had to be given up. It is now believed that the brilliancy of the color is due to the presence of oil in the feathers, this making them more translucent and bringing out the red color.[1] Water colors always become paler as the water dries out, because more light is then scattered. Some people have gone so far as to say that white pigments do not occur in nature in animals or plants;[2] but this is an over-statement. Some butterflies have a whitish pigment in their wings[3] and the silvery whiteness[4] of many fishes is due to the presence of a substance called guanin, and not to air bubbles.

Complete absorption of light gives the sensation known as black. Pulverulent silver is black because the crystals are so arranged that all the light is absorbed by reflection forward and back. This can be shown in another way. If we take a bunch of steel needles and place them with their points side by side facing the observer, the mass will appear black,[5] although we know that no single needle is black in itself. The rich color of velvet is due to its trapping the light, and the peculiar effect known as damask is due to the fibers being arranged in two different ways, so that one set absorbs more light than the other. Trees and grass may act as light traps when seen from above and they are said to look

[1] Krukenberg: Vergleichend-physiologische Studien, **1 V,** 90 (1887).
[2] Gadow: Proc. Zool. Soc., London, **1882,** 410.
[3] Hopkins: Phil. Trans., **186B,** 661 (1895).
[4] Newbigin: Color in Nature, 37, 219 (1898).
[5] Wood: Physical Optics, 449 (1911).

black to aviators.[1] If we have a material which absorbs light so completely that the powder is black, we shall get all gradations between the original color and black if we grind up such a substance, just as we got all variations between blue and white by grinding crystals of copper sulphate. If we start with yellow gold and make it more porous, it will become brown before becoming black. This happens unintentionally in the assaying of gold when a brown powder is obtained which people have thought was an allotropic form of the metal. It is merely a porous gold and when it is heated until the crystals sinter together and become less porous, the yellow color of gold reappears.

If we have very fine particles suspended in a transparent solid, liquid, or gas, these particles scatter blue light much more than they do red light, and consequently such a mass appears red by transmitted light and blue by reflected light. Skimmed milk is an instance of this sort, being distinctly bluish by reflected light and reddish by transmitted light. Tobacco smoke is blue by reflected light and red by transmitted light. The blue color of the sky is due to light which is scattered by drops of liquid or by particles of dust in the air. The intensity of the color is undoubtedly increased by the fact that we see this against the black background of infinite space. The sunset colors are due to the light which is transmitted and not scattered.

There is no blue pigment in blue eyes and it was pointed out by Tyndall[2] years ago that the blue of the eye is really the blue of turbid media, and is thus analogous to the blue of the sky or the blue of skimmed milk. At the back of the iris there is a dark pigment known as the *uvea*, which prevents the reflection of light and prevents the color of the blood from being seen. When this dark pigment is absent, we have an albino with a pink eye. The various stages between the blue and the gray eye are due to differences in the coarseness of the particles giving rise to the blue color, the blue color being the most intense the finer the particles. This is probably the reason why babies' eyes are so very blue, because the suspended particles tend to grow coarser with increasing age. All other people have a yellowish-brown pigment in the front of the iris and the combination of the struc-

[1] Luckiesh: Jour. Franklin Inst., **187,** 303 (1919).

[2] Fragments of Science: The Sky.

tural blue with the yellowish-brown pigment gives rise to the green, hazel, brown and black eyes. Except with people who have very black eyes, the pigment in the front of the iris does not develop at birth, just as the teeth do not come till later. Consequently many infants have blue eyes, which change to hazel, brown or black as they grow older, while the reverse change never occurs. Once in a while we see a man whose eyes are colored differently. This means that pigment has developed in one eye and not in the other, or that the pigment has developed unequally in the two eyes.

The green eye is due to the combination of structural blue with the pigment yellow. While this is not a common type in human beings, we get it very markedly in the case of the green tree-frog, who has no green pigment and whose green color is due to structural blue with a yellow pigment overlaying it. If we scrape the pigment layer off the back of an unfortunate frog, he turns blue. In fact, the grass-green Australian tree-frog is called *Hyla coerulea*, because he is blue when he comes to us preserved in alcohol, the alcohol having dissolved the yellow pigment.

There is a wide-spread belief that people with blue or gray eyes are better rifle shots than people with dark eyes. Since we do not see through the iris, this could not be cause and effect, though it is theoretically possible that the two characteristics might be correlated. Colonel Chamberlain has made a study of this matter and finds that of three thousand soldiers who had qualified for the grade of marksman or better, approximately two thousand had blue or gray eyes, a result which seems at first to bear out the popular belief. He finds however that of one hundred thousand white soldiers approximately two thirds have blue or gray eyes. People have made the mistake of considering absolute figures and not percentage.

If we leave out of account feathers with a blue metallic lustre, which may constitute a special case, we may say that there is no blue pigment in the feathers of any bird. This means that the blue of the kingfisher, the indigo bunting, the blue-jay, and the blue-bird, is not due to blue pigment; but is a structural color. The only pigment in the blue feathers of these birds is a dark brown one which apparently serves merely as a background, just as in the case of the blue eyes. The best explanation of the blue

feather[1] is that the horny matter is filled with an enormous number of minute air bubbles, which scatter blue light and transmit red. The blue feather is therefore the same in principle as, or the opposite in detail from, the blue sky. The color of the sky is due to the scattering of light by particles of liquid or solid suspended in a gas, the air. The blue of the feathers is due to the scattering of light by bubbles of gas, air, suspended in a solid medium. While this explanation is undoubtedly the right one, nothing analogous to a blue feather has yet been made in the laboratory. This is one of the things that people must do in the future. Apparently nobody has made any experiments to determine whether the blue light from the blue eyes and the blue feathers is polarized. This should be the case.

In this country the tufted titmouse is a gray bird with no brilliant colors; but the German titmice show great differences in color. One variety is green on the back, due to structural blue overlaid by a pigment yellow, and yellow on the belly. In another variety the brown pigment which is essential to the structural blue has not developed and the bird is consequently yellow all over. There is a third form in which the yellow pigment has not developed and the bird is therefore blue on the back and white underneath. One would like to think that the differences in color between the male and the female redstart were due to the presence in the male of a single color which was lacking in the female; but this cannot be the case, unless it can be shown that the black on the male redstart is due to a red pigment just as hematite is black in mass.

Tyndall,[2] Aitken[3] and Spring[4] consider that the color of water is blue, while Rayleigh[5] believes that the blue of the sea is merely the light reflected from the blue sky. Assuming that water is in itself blue, it would look black if no light were reflected back from the interior. A difference in the index of refraction due to difference of temperature might be sufficient;

[1] Haecker: Zool. Jahrbücher, Abt. syst. Geog. Biol. Thiere, **15,** 267 (1902).

[2] Fragments of Science: Voyage to Algeria.

[3] Proc. Roy. Soc. Edin., **11,** 472 (1882).

[4] Bull. Acad. roy. belg. (3) **5,** 55 (1883); **12,** 814 (1886).

[5] Nature, **83,** 48 (1910).

but a more usual cause is the presence in suspension of reflecting particles. If these are few in number the water will appear indigo to blue. If they are many in number we shall begin to get the yellowish to red color of light transmitted through a turbid medium and the water will appear green. Muddy waters may appear yellow or brown. As a matter of fact, the deep sea which contains little suspended matter, is blue, while near shore where there is more suspended matter, the color is often a brilliant green, especially in the tropics. The presence of air bubbles will act in the same way and in an indigo sea the crest of a wave may be green. The Lake of Constance is quite green because of the suspended calcium carbonate, while the Lake of Geneva is more blue because there is less suspended matter. The Rhine at Strasbourg is green and contains 70 percent more calcium carbonate than the blue Rhone at Geneva. The Gulf Stream is blue because there is less carbon dioxide in the warm water and consequently less calcium carbonate. The clear brown color of some New England brooks is probably due to the presence of tannin-like materials.

The colloidal metals are a special and very interesting case of the colors of colloidal solutions. Colloidal gold solutions[1] can be prepared which are red, violet or blue by transmitted light; and colloidal silver solutions[2] which are yellow, red or blue. In general the blue gold solutions contain coarser particles than the red ones, but this is not always true. The peculiarities in the colors of colloidal metals seem to be connected intimately with the fact that the metals show selective reflection. In the case of selective reflection, some or all of the light which is adsorbed very strongly by a given substance is reflected strongly from a polished surface of that substance. The surface color of magenta is green, while the body color or the color due to the transmitted light is red. With indigo the surface color is red and the body color blue. The surface color is believed to be due to resonance, the substance emitting the rays which it adsorbs very strongly. It seems probable that a very small granular particle might emit surface color by resonance on the opposite side from the source of light, in which case we should have the surprising phenomenon

[1] Faraday: Phil. Trans., **147,** 145 (1857).

[2] Carey Lea: Am. Jour. Sci. (3) **37,** 475 (1889).

of a substance apparently transmitting the light which it adsorbs most strongly. On the other hand, the amount of reflection from the back surface of a particle of the light ordinarily transmitted will be greater, the less the thickness of the particle. Consequently, with fine particles there will be a more or less complete reversal of the usual colors. The light which is ordinarily reflected selectively will be transmitted by resonance, while the light which is ordinarily transmitted is scattered.

This is known to be true for indigo and for gold. Colloidal indigo solutions transmit red light and not blue. Massive gold reflects yellow when compact and brown to black when porous. Particles which do not resonate are yellow or brown by reflected light and transmit blue light. Massive gold is red by multiple reflection and thin films are green by transmitted light.[1] Colloidal solutions when containing very fine particles reflect green and transmit red. In the red gold solutions the particles are green, while they are yellow to brown in the blue solutions. The violet solutions are a mixture of red and blue solutions. A thin film of gold does not resonate readily and consequently transmits green light. If heated, it becomes granular and then transmits purple light. Gelatine films containing gold may be red by transmitted light when moist and blue when dry. The contraction due to drying brings the particles of gold sufficiently near together to be equivalent to reversible agglomeration, thereby destroying the resonance. In a colloidal gold solution a single particle of a given size might resonate and transmit red light, while a cluster of finer particles might not resonate and would therefore transmit blue light. This is probably the explanation for some of the abnormal results observed.

Silver reflects yellow after multiple reflection, while with fewer reflections the light is said to be red.[2] A very fine colloidal solution transmits yellow and scatters blue, while somewhat coarser particles transmit red and are blue by reflected light. The coarsest colloidal silver does not resonate and consequently is yellow by reflected light, transmitting blue light. This is exactly what should happen on the facts as stated. The pink color in a given sample of white lead was shown by

[1] Beilby: Proc. Roy. Soc., **72**, 226 (1903).

[2] Regnault-Betton: Elements of Chemistry, 366 (1874).

Baker[1] to be due to silver, which was probably present as colloidal silver. The colors of Carey Lea's photohalides are known to be due to colloidal silver[2] and the difference in the color of photographic plates[3] with different developers is due to the degree of fineness of the precipitated silver.

Colloidal platinum[4] has been obtained blue, green, yellow, red, brown and black; but there are no data which will enable us to discuss these colors satisfactorily.

Owing to differences in the variation of the absorption with varying thickness of the absorbing agent, a substance may be one color in thin films and another in thicker masses. Thin layers of a cyanine solution appear blue and thick layers red,[5] and the same is true of cobalt glass. Potassium ferricyanide is a brown-red in coarse crystals and yellow when powdered. Andersen[6] has shown that thin plates of hematite (0.1μ) are yellow by transmitted light, the color varying with increasing thickness through reddish brown to deep brown red or blood red. An anhydrous, yellow ferric oxide is said to be obtained by the oxidation of ferric sulphide[7] and we get yellow bricks on burning a highly calcareous clay even though the iron content is higher than that which would give a red clay if the lime were not present.[8] It seems probable that the ferric oxide is present in such a fine state of subdivision that it is yellow and not red. Mott[9] has prepared both red and yellow ferric oxide by volatilization of iron in the electric arc, the yellow being the finer powder. Addition of a liquid having approximately the same index of refraction as yellow ferrocyanide or yellow rouge should make

[1] Phil. Mag. (4) **37,** 344 (1869).

[2] Carey Lea: Am. Jour. Sci. (3) **33,** 349, 489 (1887).

[3] Lüppo-Cramer: Zeit. Kolloidchemie, **7,** 99 (1910); **8,** 240 (1911); Chapman Jones: Phot. Jour., **51,** 159 (1911).

[4] Garbowski: Ber. deutsch. chem. Ges., **36,** 216 (1903); Gutbier: Zeit. Kolloidchemie, **5,** 50 (1909); Wöhler and Spengel: Ibid., **7,** 243 (1910); Bredig: Zeit. phys. Chem., **31,** 258 (1899)

[5] Wood: Physical Optics, 438 (1911).

[6] Am. Jour. Sci. (4) **40,** 370 (1915).

[7] Diamond: Jour. Soc. Chem. Ind., **37,** 451 R (1918).

[8] Keane: Jour. Phys. Chem., **20,** 734 (1916); Scheetz: Ibid., **21,** 570 (1917).

[9] Trans. Am. Electrochem. Soc., **34,** 292 (1918).

the powder more transparent and redder. Experiments by Schenck[1] on the precipitation of hydrous copper and aluminum oxides make it seem probable that cupric oxide is blue in thin films and not black. Mott obtained a brilliant blue by volatilizing a mixture of equal parts of manganese and copper.

Electrical Properties

If a particle suspended in a liquid adsorbs a free ion, the charged particle will then behave to some extent like an ion and will tend to move under electrical stress toward the cathode if the adsorbed ion is positive and toward the anode if the adsorbed ion is negative.[2] Reference has been made to the fact that silver bromide particles move to the cathode when stabilized by silver ions and to the anode when stabilized by bromine ions. By following the electrolysis under the microscope it is possible to determine the rate of movement of a suspended particle for a given difference of electrical potential. The rate of migration of colloidal particles is of the same order as that of ions.[3] Thus colloidal silver moves with a velocity of 2.0–3.8μ/sec. under a potential drop of one volt per centimeter, and colloidal gold at about 4.0μ/sec., while the chlorine ion gives a value of 6.8μ/sec.

Billitzer[4] has attempted to determine absolute potential differences by finding solutions in which a given colloidal metal did not move under electrical stress. While the method is good in principle, one cannot reason from the adsorption of a finely divided metal to the adsorption of massive metal. It seems possible that definite results might be obtained if the problem were attacked with a better knowledge of colloid chemistry. Since the colloidal particle moves in one direction with reference to the water, the water moves in the opposite direction relatively to the particle. This can be shown if we keep the colloidal particles stationary in the form of a diaphragm.

The electrical transfer of particles through the liquid is called cataphoresis and the transfer of liquid through a stationary diaphragm is called electrical endosmose. It was first observed by

[1] Jour. Phys. Chem., **23,** 284 (1919).

[2] See Linder and Picton: Jour. Chem. Soc., **71,** 568 (1897).

[3] Zsigmondy: The Chemistry of Colloids, 46 (1917).

[4] Drude's Ann., **11,** 902, 927 (1903).

Reuss at Moscow in 1808. Working with so-called pure water it is found that water passes to the cathode when the porous diaphragm is made of glass, shellac, earthenware, carborundum, asbestos, wool, cotton, platinum, silver, arsenic sulphide, or sulphur; and to the anode when the diaphragm is chromic chloride, cobalt oxide, zinc oxide, or barium carbonate.[1] When turpentine was substituted for water, it moved to the anode with all diaphragms except sulphur. Coehn[2] has attempted to account for this by postulating empirically that when two non-miscible substances are in contact, one being a pure liquid, the substance with the higher dielectric constant is charged positively with reference to the one with the lower dielectric constant. This rule applies in the case of water and turpentine where the dielectric constants are 81 and 5 respectively, but it is by no means absolute even for pure liquids,[3] and breaks down completely when applied to aqueous solutions. The phenomenon depends on the relative adsorption of ions and Coehn's rule is a useful first approximation in certain cases.

The first quantitative study of electrical endosmose with solutions was made by Wiedemann[4] who deduced two empirical generalizations:

1. The mass of liquid transported through a porous diaphragm in a given time is directly proportional to the current. For a given diaphragm material and given current, the amount is independent of the length and cross-section of the diaphragm.

2. For a given diaphragm material the difference in hydrostatic pressure maintained between the two sides of a porous diaphragm is proportional to the applied potential and is independent of the dimensions of the diaphragm.

Helmholtz[5] considers that under most circumstances liquids and solids become charged electrically when brought into contact, the surface of the solid having the opposite charge from that of the liquid in contact with it, thus giving rise to a so-called

[1] Quincke: Pogg. Ann., **107,** 1 (1859); **110,** 38 (1860). Actually Quincke forced water through the diaphragms and noticed the charge.

[2] Wied. Ann., **64,** 227 (1898); Zeit. Elektrochemie, **16,** 586 (1910).

[3] Briggs: Jour. Phys. Chem., **21,** 204 (1917).

[4] Pogg. Ann., **87,** 321 (1852); **99,** 177 (1856).

[5] Wied. Ann., **7;** 337 (1879).

double layer. If the solid cannot move because it is a capillary tube or a diaphragm, the introduction from outside of a potential gradient will tend to cause a displacement of the electrically charged layer of liquid. If the liquid is not a perfect insulator, the displacement results in a continuous flow of liquid along the surface of the solid.[1] Since the movement of a suspended and electrically charged particle is in accord with Faraday's law and Kohlrausch's law, it follows that the movement of water relatively to the diaphragm will not be.

Freundlich[2] has deduced an equation for the amount of liquid V transported in unit time through a porous diaphragm:

$$V = \frac{q\epsilon ED}{4\pi\eta l}$$

E is the total potential drop through the diaphragm, D is the dielectric constant and η the viscosity coefficient of the liquid, ϵ is the potential of the Helmholtz double layer at the solid-liquid interface, q is the cross-section and l the thickness of the diaphragm. If γ is the specific resistance of the liquid, then the total resistance, R, of the diaphragm will be $l/\gamma q$. Substituting for E by means of Ohm's law we may write the equation

$$V = \frac{\epsilon CD}{4\pi\eta\delta}$$

For a given liquid and diaphragm at constant temperature, ϵ, η, γ and D are constant, so that V is proportional to the current and the term for the diaphragm disappears. This is Wiedemann's first empirical generalization. The other can be deduced by introducing an expression for the hydrostatic pressure.

Since the charge on the diaphragm depends on the nature of the ion adsorbed, it follows that an aqueous solution may flow one way or the other through a given diaphragm, depending on the nature of the dissolved substance. This was brought out clearly by Parker[3] and was emphasized by Perrin,[4] who found a reversal in many cases when the solutions were alkaline instead of acid.

[1] Lamb: Phil. Mag. (5) **25,** 52 (1888).

[2] Kapillarchemie, 226 (1909).

[3] Johns Hopkins Dissertations, **31,** 23 (1901); Briggs: Jour. Phys. Chem., **21,** 235 (1917).

[4] Jour. Chim. phys., **2,** 601 (1904).

Every diaphragm tends to become charged positively in an acid solution and negatively in an alkaline solution. Every ion of unlike sign tends to neutralize the charge on the diaphragm. Perrin believed that the effect of other ions was more marked the greater the valence; but this is true only in so far as the ion with the higher valence is adsorbed more strongly than the ion with a lower valence,[1] in other words, in so far as Schulze's so-called law holds. In some cases the agreement is very good. Thus in acid solutions, the flow through the diaphragm to the anode increases as the anion changes from quadrivalent ferrocyanide to bivalent sulphate to univalent chloride, because the adsorption of the anion decreases in the same order and the diaphragm becomes charged more positively. In alkaline solution the flow to the cathode increases as the cation changes from trivalent lanthanum to bivalent barium to univalent sodium. On the other hand, with a porous cup in a slightly acidified copper sulphate solution the flow is to the cathode, apparently because copper ions are not adsorbed to any great extent, while the adsorption of sulphate ions exceeds the adsorption of hydrogen ions because the concentration of the first is so much greater than that of the second. With a slightly acidified copper nitrate solution the flow is to the anode, because the nitrate ions are not adsorbed very much and the hydrogen ions determine the direction of the flow.

Much to Perrin's surprise a barium carbonate solution acted in one case as though it were an acid. This is undoubtedly because of the preferential adsorption of barium ions which charge the diaphragm positively.

In electrolytic reductions of organic substances in aqueous alcoholic solutions using a porous cup, the flow of liquid to the cathode may be quite annoying. Owing to the lower dielectric constant of alcohol, the normal tendency of the liquid to go to the cathode becomes less, but the increased resistance would increase the flow and nothing is known in regard to adsorption from these solutions. Billitzer[2] found that colloidal platinum is charged positively in aqueous alcohol though negatively in pure water.

[1] Elissaroff: Zeit. phys. Chem., **79,** 285 (1912).
[2] Zeit. phys. Chem., **43,** 312 (1903).

The amount of liquid transferred by electrical endosmose increases with rising temperature, the increase being nearly proportional to the change in the fluidity[1] (the reciprocal of the viscosity). This would follow from Freundlich's equation if one assumes that D and ϵ change but slightly over the temperature range.

The commercial applications of electrical endosmose have not been very successful. Count Botho Schwerin[2] took out a number of patents for removing water from peat. Starting with a peat mud containing about 90 percent moisture, he claimed that the moisture content could be reduced to 65 percent at an expenditure of about 15 kw.-hr. per cubic meter of water removed, the best potential gradient being 4–5 volts per centimeter. The cost of drying from 65 percent moisture to 20 percent moisture was so great that the process was not a success. It is reported that electrical endosmose has been used successfully in the dye industry in the drying of pastes. Electrical tanning has also been tried, the tanning liquor being carried into the hides by electrical endosmose. This seems to have failed in part on account of the oxidation of the tannin at the anode. Cataphoresis is made use of in electrolytic refining and plating, the use of addition agents being essential in some cases.[3]

There are no very definite results as to the effect of colloids on the conductance of solutions,[4] but it is evident that an adsorbed ion cannot have as high a migration velocity as an unadsorbed ion, and that consequently the presence of a colloid must decrease the conductance to some extent, depending on the amount and nature of the ions adsorbed. If a clay suspension is stirred,[5] the conductance may increase because the adsorbed ions which are carried down when the suspension settles are brought up between the electrodes. McBain[6] found that certain solutions of sodium palmitate conducted well, although the

[1] Briggs, Bennett and Pierson: Jour. Phys. Chem., **22**, 256 (1918).
[2] Zeit. Elektrochemie, **9**, 739 (1903).
[3] Müller and Bahntje: Zeit. Elektrochemie, **12**, 317 (1906).
[4] Wo. Ostwald: Van Bemmelen Gedenkboek, 267 (1910).
[5] Bleininger: Trans. Am. Ceramic Soc., **15**, 343 (1913).
[6] Jour. Chem. Soc., **105**, 965 (1914); Jour. Am. Chem. Soc., **42**, 426 (1920).

freezing points of the solutions were only enough to account for the sodium ions. He assumes that the palmitate ions polymerize to large hydrated units which he calls micelles and which he considers colloidal and to which he applies Stokes' law although he does not state specifically why or how the polymerized ions separate as a second phase. It is probable that we have hydrolysis to caustic soda and colloidal palmitic acid, the latter[1] then adsorbing hydroxyl ions, just as we know that silicic acid adsorbs hydroxyl ions and is peptized by them. This suggests an interesting theoretical possibility. Suppose we have two sets of finely divided particles neither of which adsorbs the other appreciably and let us also suppose that one set of particles adsorbs a given cation very strongly while the other set of particles adsorbs a given anion very strongly. If we take a mixture of these two sets of particles and add a small amount of the salt of the given base and the given anion, we shall have a colloidal solution which will conduct electricity very well but which will contain no free ions to speak of because, by definition, the cations have been practically completely adsorbed by one set of particles and the anions by the other set of particles. It is not known whether these limiting conditions can all be fulfilled simultaneously. A possible case would be the mixing of dilute solutions of silver sulphate and lead chloride. The lead sulphate would adsorb sulphate or lead ions strongly and the silver chloride would adsorb chloride or silver ions strongly. Nobody knows what each would do to the other.

While an adsorbed ion may increase the conductance of a liquid, it will behave quite abnormally as regards electrometric measurements. An adsorbed chlorine ion will not give a test with silver nitrate and consequently will have only a negligible effect on a chlorine electrode. It is not probable that an adsorbed hydrogen or hydroxyl ion behaves electrometrically like a free hydrogen or hydroxyl ion. This possible error has been overlooked in many cases where the hydrogen electrode has been used. Another source of error in electrometric measurements with colloidal solutions is to neglect the fact that we are not dealing with true solutions. If we measure a copper electrode in a solution of alkaline copper tartrate we find that the concen-

[1] There may also be adsorption by colloidal sodium palmitate.

tration of copper ions is extremely low. That is all that the measurement tells us. If the copper is in true solution, it must be present as a complex salt, as is unquestionably the case with potassium silver cyanide. If we have peptized copper oxide or hydroxide present, there is no need to assume the existence of a complex copper salt at all. The true interpretation of the phenomena cannot be made until we know whether a so-called alkaline copper tartrate solution is a true solution or not. We cannot answer this question at present. On the other hand, it seems practically certain that the effect of sugars in preventing the precipitation of the heavy metal hydroxides by alkalies is due to the formation of colloidal solutions. Consequently the conclusions drawn from electrometric measurements of such solutions are necessarily false.

Stability of Colloidal Solutions

1. Sols stabilized by Ions.—Three classes of colloidal solutions have been distinguished, in which the stabilization is due: to adsorbed liquid; to an adsorbed undissociated substance which may be in true solution or may be itself in colloidal solution; and to an adsorbed ion. The last case is the simplest theoretically and the most varied experimentally. So long as the particles are all charged positively or all charged negatively, they will tend to repel each other and will not coalesce unless the concentration is too high. If the charge is neutralized or counterbalanced in any way, the particles will agglomerate[1] unless some other factor comes into play. Such colloidal solutions will therefore be very sensitive to electrolytes having a readily adsorbed ion of the opposite charge from that which stabilizes the colloidal solution. Colloidal solutions which are peptized by the liquid will be relatively insensitive to electrolytes because these will act only in so far as they decrease the peptizing action of the liquid. The second case is intermediate with reference to the other two and its properties will vary between those of the other two types.

We will consider first the case in which the colloid is stabilized

[1] Hardy: Zeit. phys. Chem., **33,** 285 (1900); Burton: Phil. Mag. (6) **12,** 472 (1906); **17,** 583 (1909).

chiefly or entirely by the presence of an adsorbed ion. Such solutions precipitate completely at the iso-electric point, as it is called, where the electrical charge is neutralized or counterbalanced. If a suspension is stabilized by the preferential adsorption of hydrogen ion from hydrochloric acid solution, the solution contains free hydrogen ions, free chlorine ions, and the adsorbed hydrogen ions which make the suspension behave like a cation though with a different migration velocity from that of hydrogen. If the suspension is made to adsorb an anion in an amount equivalent to the hydrogen ion adsorbed, the suspended particles will be electrically neutral. This can be done by adding an electrolyte with a readily adsorbed anion. Since this is a matter of selective adsorption, the concentration of the added anion necessary to cause an adsorption equivalent to the hydrogen adsorption will vary with each anion. To put the matter more generally, the amount of an electrolyte necessary to precipitate a colloidal solution will vary with the nature of the cation, the anion, and the dispersed phase. While it is generally true that an ion of higher valence will be adsorbed more strongly than one of lower valence, this so-called law of Schulze[1] is only a first approximation and should be considered only as a guide.

That some univalent ions are adsorbed more strongly by some substances than some bivalent or trivalent ions is shown clearly in data by Odén[2] on colloidal sulphur, given in Table XLIII. In the second column are the liminal concentrations necessary to coagulate the sulphur, given in gram ions per liter of the cations; in the third column are given the reciprocals of these values, the so-called ionic precipitating power.

Under the conditions of Odén's experiments, sulphur is a negative colloid and the precipitation is therefore due to an adsorption of cations. The first thing to be noticed is that hydrogen ion is not adsorbed strongly by sulphur, the precipitating power of hydrochloric acid being much less than that of lithium, ammonium, sodium, potassium, rubidium, or caesium chloride. Instead of these univalent cations precipitating at the same concentration, the required concentration of lithium chloride is in round numbers one hundred times that of caesium

[1] Jour. prakt. Chem. (2) **25,** 431 (1881); **27,** 320 (1884).

[2] Der kolloide Schwefel, 156 (1912).

TABLE XLIII.—COAGULATION OF SULPHUR AT 18°–20°

Salt	Liminal value gram-ions cations per liter	Ionic precipitating power of cation
HCl	6.0	0.16
LiCl	0.913	1.1
NH_4Cl	0.435	2.3
$(NH_4)_2SO_4$	0.600	1.7
NH_4NO_3	0.506	2.0
NaCl	0.153	6.1
Na_2SO_4	0.176	5.7
$NaNO_3$	0.163	6.1
KCl	0.021	47.5
K_2SO_4	0.025	39.7
KNO_3	0.022	45.5
RbCl	0.016	63.0
CsCl	0.009	108.0
$MgSO_4$	0.0093	107.5
$Mg(NO_3)_2$	0.0080	125.0
$CaCl_2$	0.0041	245.0
$Ca(NO_3)_2$	0.0040	247.0
$Sr(NO_3)_2$	0.0025	385.0
$BaCl_2$	0.0021	475.0
$Ba(NO_3)_2$	0.0022	461.0
$ZnSO_4$	0.0756	13.2
$Cd(NO_3)_2$	0.0493	20.3
$AlCl_3$	0.0044	227.0
$CuSO_4$	0.0098	102.0
$Mn(NO_3)_2$	0.0096	105.0
$Ni(NO_3)_2$	0.0446	22.4
$UO_2(NO_3)_2$	0.0137	73.0

chloride. The liminal values for barium and strontium are nearly equal, but calcium chloride requires a distinctly higher concentration. If we take the different bivalent ions the values range from 0.0756 for zinc to 0.0022 for barium, a ratio of over thirty to one. The univalent caesium ion has a greater precipitating power than the bivalent zinc, cadmium, nickel, and uranyl ions; and about the same precipitating power as the bivalent copper, manganese, and magnesium ions. The trivalent aluminum ion has about the same precipitating power as the bivalent calcium ion and distinctly less precipitating power than bivalent strontium and barium ions. The specific nature of the adsorp-

tion comes out extraordinarily clearly with sulphur, about the only orthodox thing being that nitrate, chloride, and sulphate behave practically alike, though even here Odén considers that sulphate has a slight protecting action. This specific nature appears more clearly perhaps if we arrange the cations in order, the one with the greatest precipitating power coming first: Ba, Sr>Ca, Al>Mg, Cs, Mn, Cu>UO_2>Rb>K>Ni, Cd, Zn>Na>NH_4>Li>H.

Sulphur is admittedly an extreme case, but Freundlich[1] gives data for colloidal platinum from which I deduce the order: Al, Pb>Ba, UO_2>Ag>K, Na. Bivalent lead has practically the same precipitating power as trivalent aluminum. Univalent silver is nearer to bivalent uranyl and barium than to univalent potassium and sodium. If more cations had been studied we should very likely have got more distinct evidence of specific action. As it is, it takes 130 millimols NaOH per liter to coagulate the platinum and only 2.5 millimols NaCl. The change from chloride to hydroxide has a more marked effect than the change from sodium to barium. It seems very probable that barium hydroxide would have no greater precipitating power than sodium chloride. From Pappadà's experiments with colloidal silver[2] I deduce the following order of adsorption: Al>Ba, Sr, Ca>H>Cs>Rb>K>Na>Li. From these data Pappadà concludes that the migration velocity is the determining factor with the univalent cations; but this cannot be true. The difference between aluminum and hydrogen is not very great, one drop of M/10 HCl producing a coagulation and one drop M/20 $AlCl_3$. In tenth-normal solutions potassium iodide, nitrate, and sulphate produce no coagulation. The reason given by the author is that these anions react with the colloidal silver. In normal solutions the iodides, nitrates, and sulphates are said to precipitate at the same concentrations as the corresponding chlorides and bromides. The effect of concentration is a little obscure in other respects, since 5 or 6 drops of normal KCl precipitate 2 cc 0.06 percent Ag, whereas it takes only 30 drops N/10 KCl to produce precipitation. The essential thing is that the different univalent cations have different liminal values; the

[1] Kapillarchemie, 352 (1909).

[2] Pappadà: Gazz. chim. ital., **42** I, 263 (1912).

difference between hydrogen and lithium is greater than that between hydrogen and aluminum. Experiments might well have been made with barium hydroxide and with the sodium salts of organic acids. Freundlich and Leonhardt[1] find that with the negative colloid, $MoO_2.H_2O$, caesium is two hundred times as effective as lithium, and barium four times as effective as calcium.

TABLE XLIV.—COAGULATION OF MASTIC

Salt	Liminal value gram atoms	Ionic precipitating power of cation
$NaCl$	1.0	1
$AgNO_3$	0.125	8
$HgNO_3$	0.00125	800
HCl	0.010	100
$CaCl_2$	0.025	40
$BaCl_2$	0.025	40
$ZnSO_4$	0.050	20
$Al_2(SO_4)_3$	0.0004	2500
$Al_2(NO_3)_3$	0.0004	2500
$FeCl_3$	0.0003	3300

From experiments on mastic[2] we get the data given in Table XLIV. If we consider the mercury in mercurous nitrate as a univalent ion, it is very much out of place, precipitating at much lower concentrations than the barium, calcium and zinc salts. Of course the formula should be written $Hg_2(NO_3)_2$ with Hg_2 as a bivalent ion.[3] In this case the precipitating power becomes 1600 instead of 800, which puts it up much nearer the trivalent cations than the bivalent ones. The order of cations is: Fe, $Al > Hg_2 > H > Ba$, $Ca > Zn > Ag > Na$. Only three anions are given in the table, so it is impossible to tell what effect the anions have. A good many experiments have been made on mastic with different acids but the degree of electrolytic dissociation varies so as to make these results inconclusive. With Prussian blue Pappadà[4] found the order of the cations to be: Fe, Al, Cr >

[1] Kolloidchemische Beihefte, **7**, 172 (1915).
[2] FREUNDLICH: Kapillarchemie, 367 (1909).
[3] OGG: Zeit. phys. Chem., **27**, 285 (1898).
[4] Zeit. Kolloidchemie, **6**, 83 (1911).

Ba, Cd > Sr, Ca > H > Cs > Rb > K > Na > Li. Sulphates, nitrates, chlorides, bromides, and iodides all behaved alike. Practically the same order of the cations was obtained for copper ferrocyanide.[1] In the cases studied by Pappadà the specific adsorption appears to play a very small part. The data for arsenic sulphide,[2] however, give variety enough. The order of cations is: Ce, In, benzidine, Al > new fuchsine, crystal violet > quinine > morphine, UO_2, Sr, Ca > Be, Zn, Ba > Hg > p-chloraniline, toluidine > aniline > strychnine > guanidine > H > K > Na > Li. The organic cations come in where they please and play havoc with any rule as to valency. The chlorides and nitrates give practically the same values and the sulphates are not far out of line, though it seems probable that the restraining power of sulphate is rather greater than that of chloride or nitrate. The liminal values in gram molecules of the cation per liter are 0.0056, 0.0066, 0.0086, 0.110 and 0.240 for potassium nitrate, sulphate, formate, acetate, and citrate, from which one can deduce that the order of adsorption of anion is: citrate, acetate, formate, sulphate, nitrate, chloride. It is a great pity that Freundlich did not try other combinations, such as barium acetate for instance. Addition of amyl alcohol or of phenol makes the arsenic sol more susceptible to univalent and trivalent cations[3] and less sensitive to bivalent and quadrivalent cations, but we do not know why.

From the experiments on hydrous ferric oxide,[4] the order of adsorption of the precipitating anions appears to be $Cr_2O_7 > SO_4 > OH >$ salicylate > benzoate > formate > Cl > No_3 > Br > I, while the order for the cations is: H > Ba > Mg > Tl, Na > K. The univalent ions do not all behave alike and neither do the bivalent ones; but the upholders of Schulze's law can comfort themselves with the fact that the two sets do not overlap except in the case of hydrogen. There is no such comfort in the case of albumin. The probable order of adsorption of anions, so far as known, is: sulphocyanate, iodide > chlorate > nitrate > chloride

[1] Pappadà: Zeit. Kolloidchemie, **9**, 136 (1911).

[2] Freundlich: Kapillarchemie, 351 (1909); Freundlich and Schucht: Zeit. phys. Chem., **80**, 564 (1912).

[3] Kruyt and Duin: Kolloidchemische Beihefte, **5**, 269 (1913).

[4] Freundlich: Kapillarchemie, 352, 358 (1909); Zsigmondy: Kolloidchemie, 181 (1912); Pappadà: Zeit. Kolloidchemie, **9**, 233 (1911).

> acetate > phosphate > sulphate > tartrate, the sulphocyanate ion being adsorbed the most and the tartrate ion the least. Here there is nothing even to suggest Schulze's law and the firm belief which most people have in Schulze's law is probably one reason for the marked failure to account satisfactorily for the phenomena with albumin. With the cations albumin appears to be fairly orthodox for the order of adsorption appears to be: Th, UO_2 > Cu, Zn > Ca > Mg > Li > K, Na > NH_4, though even here the lithium stands higher in the series than it has been found with other substances.

Weiser and Sherrick[1] have measured the adsorption of ions by barium sulphate and find that the order is: ferrocyanide > nitrate > nitrite > chlorate > permanganate > ferricyanide > chloride > bromide > cyanide > sulphocyanate > iodide, the ferrocyanide ion being adsorbed the most and the iodide ion the least. The above order is obtained when the concentrations are given in gram equivalents. If they are taken as gram molecules, ferrocyanide moves down between the chlorate and permanganate, and the ferricyanide between the chloride and bromide. On either method of tabulation the trivalent ferricyanide ion is adsorbed very much less than some of the univalent ions. The difference for different univalent ions is very great, 100 mols of barium sulphate taking up about 8.5 mols of nitrate as against about 0.06 of iodide.

Weiser and Middleton[2] have determined the order of precipitation of colloidal ferric oxide by different anions and obtain results which agree with the previous data in so far as they deal with the same electrolytes, the order being: dichromate > tartrate > sulphate > citrate > oxalate > iodate > phosphate. They have also determined the amount of adsorption when ferric oxide is precipitated in presence of a definite excess of salt. This order is quite different, being: phosphate > citrate > tartrate > oxalate > sulphate > iodate > dichromate. The reason for the discrepancy is apparently that there is an adsorption of the electrically neutral salt in addition to the ion adsorption. If this is selective, it may change the order to any extent and apparently does change it very much in this case. The difficulty with this is that it

[1] Jour. Phys. Chem., **23**, 205 (1919).
[2] Ibid., **24**, 30 (1920).

leaves us with no independent proof that the order of precipitation is really the same as the order of adsorption of the ions. This confirmation will undoubtedly be furnished some day; but, until it is, the connection between adsorption and precipitation can only be considered as extremely probable but as not proved. What we actually measure is the adsorption necessary to cause precipitation plus the adsorption by the precipitated substance. This latter item can theoretically be made as small as one pleases by adding only enough electrolyte to precipitate an infinitely small amount of the colloid; but the errors of analysis then become very large.

While there is unquestionably a tendency for ions of a higher valence to be adsorbed more strongly than ions of a lower valence, the experiments which have been cited show that there are many exceptions[1] and that the fundamental rule is that the adsorption is specific both as regards the adsorbing substance and the ion adsorbed.

Albumin is a specially interesting case because it is peptized readily by cations or anions. When it is negatively charged, as in a slightly alkaline solution, a strongly adsorbed anion will make it more negative and more stable. Consequently precipitation by a sodium salt will be more effective the less readily the anion is adsorbed. On the other hand, in acid solutions the sodium salt with the most strongly adsorbed anion will be the most effective in causing precipitation. Negatively charged albumin is precipitated readily by sodium chloride and not at all by sodium iodide, while positively charged albumin is precipitated by sodium iodide much more readily than by sodium chloride. Potassium iodide[2] has more effect than potassium chloride with Rhodamine B while the reverse is true with wool violet S.

Caseine has not been studied so intelligently as albumin and the results are consequently less clear. Caseine is insoluble in water but reddens litmus paper and sets free carbon dioxide from carbonates and bicarbonates. It is therefore usually considered an acid whereas the phenomenon is really due to a marked adsorption of the base. Owing to adsorption, indicators are usually unreliable in protein solutions as a means of determining hy-

[1] See also Mines: Kolloidchemische Beihefte, **3,** 212 (1912).

[2] Traube: Kolloidchemische Beihefte, **3,** 241 (1912).

drogen ion concentration. Like albumin, caseine is carried into apparent solution by acids, alkalies, alkaline earths, and some salts. It is also peptized by caffeine, strychnine, etc.[1] The so-called solutions are opalescent and the caseine can be removed by ultrafiltration, showing that it is not in true solution. As one might expect, the peptizing action of the alkaline earths is less marked than that of the alkalies, because the adsorption of the bivalent cations cuts down the peptizing action of the hydroxyl. When peptized by hydroxyl, caseine is precipitated by solutions of calcium chloride, barium chloride, magnesium sulphate, zinc sulphate, copper sulphate, and alum. In these cases it seems probable that the negative charge is neutralized by the readily adsorbed cations. On the other hand, when peptized in acid solution, salts cause precipitation in the following order: $ZnCl_2 > KBr > CuCl_2 > MnCl_2$. There is no apparent reason for this and there must be experimental error somewhere. In fact the whole behavior of caseine in presence of salts needs careful revision because the present data are quite unsatisfactory.

Colloidal silicic acid behaves like caseine in one respect, that it adsorbs lime from suspended calcium carbonate. In accordance with this is the fact that silicic acid, though peptized by caustic soda or ammonia, is precipitated by barium hydroxide because of the marked adsorption of the alkaline earth cation. It is also precipitated by alum and by basic dyes, which is as it should be.

With colloids stabilized by an electrical charge, we find that the amount of any salt necessary to produce precipitation varies with the way in which it is added, more being necessary if the salt solution is added slowly. The explanation of this seems to be that the first addition of salt causes a slight agglomeration which is not enough to cause precipitation, but which cuts down the adsorbing power of the colloid, so that more salt is necessary to cause the same adsorption. It is also true that a change in the adsorbing power of a colloidal substance will affect its stability. If we have anhydrous ferric oxide on the one hand and hydrous ferric oxide on the other, without specifying at present what we mean by hydrous, we shall expect to

[1] Osborne: Jour. Physiology, **20**, 399 (1910); Van Slyke and Publow: Science and Practice of Cheese-making, 142 (1913).

have different degrees of stability in the two cases and so we do. Two colloidal ferric oxides have been distinguished and we speak of colloidal solutions of alumina and metalumina, tungstic acid and metatungstic acid, stannic and metastannic acid, etc., where our only real criterion is the difference in stability. Stannic acid is peptized by dilute HCl, HNO_3, H_2SO_4 and alkalies while metastannic acid is soluble in HCl, insoluble in HNO_3, and swells in H_2SO_4. As a matter of fact one can have a whole series of stannic acids.[1] It is merely a question of how carefully one differentiates properties. By rapid dialysis of silicic acid solutions it is possible to get much higher concentrations than by dialysis because the silicic acid changes less.[2]

With a colloidal solution stabilized by an adsorbed ion, the reversibility of the coagulation depends upon the possibility of washing out the precipitating agent and on the physical state of the precipitate. The more strongly the precipitate is adsorbed the more difficult it will be to wash it out. When albumin is precipitated by sodium chloride, the coagulation is ordinarily reversible. When it is precipitated by the salt of a heavy metal, the coagulation is irreversible. All precipitates tend to change on standing, becoming coarser or more firmly agglomerated. It may then happen that washing out the precipitating agent will not cause peptization. When albumin is precipitated by calcium chloride, the coagulation is reversible if the calcium chloride is washed out at once; but is not reversible if the precipitate is allowed to stand. If a precipitate of silver chloride be allowed to stand over night, it can then be filtered and washed much more satisfactorily than when first precipitated.

The effect of temperature changes on the stability of a colloidal solution may be two-fold. Raising the temperature will increase the peptizing action of the solvent thereby increasing the stability, or it may decrease the adsorption of the stabilizing ion, thus making the solution less stable. The second factor is the more important with colloidal solutions stabilized by an adsorbed ion.[3] Thus albumin solutions coagulate on heating

[1] Vignon: Jour. Chem. Soc., **56,** 833 (1889); Mecklenburg: Zeit. anorg. Chem., **74,** 207 (1912).

[2] Zsigmondy: Van Bemmelen Gedenkboek, 7 (1910).

[3] Linder and Picton: Jour. Chem. Soc., **87,** 1931 (1905).

and so do caseine solutions. When a solution is actually frozen solid, we have the possibility of the colloid agglomerating. If it does that, the colloidal solution will not be formed when the mass melts; but otherwise it may. The experiments along this line are not very satisfactory because they were done without any knowledge of the general theory.[1] The main result is about what one would expect. In presence of a very small amount of peptizing agent, the precipitation is likely to be irreversible because the precipitate agglomerates on standing. If there is a fair excess of peptizing agent, the precipitation will be reversible. This is of course especially true if the peptizing agent is a water-soluble colloid. Ehrenberg[2] considers that the pressure due to the expansion when water freezes may be a factor in causing coagulation.

Where the adsorption is very low, it may require a very high concentration of a given ion to cause peptization. This occurs in a number of cases of peptization by alkalies and is probably another reason why people have considered that alkali salts were formed and not colloidal solutions.

If one over-runs the point of electrical neutrality, the suspension may become stable again because it is stabilized by preferential adsorption of an ion having the opposite sign. If one adds a little less than the equivalent amount of a dilute potassium bromide solution to a dilute silver nitrate solution, one gets a positively-charged colloidal solution of silver bromide because the silver bromide is stabilized by adsorbed silver ions. If one adds slightly more than the equivalent amount of the potassium bromide solution, there is obtained a negatively-charged colloidal solution of silver bromide, stabilized by adsorbed bromine ions. If more bromide solution is added, the silver bromide will coagulate because there will come a point at which the slight adsorption of the potassium ion counter-balances the adsorption of the bromine ion. In other words, silver bromide precipitates when there is a distinct excess of silver nitrate, stays in suspension as a positively charged colloid when there is only a slight excess of

[1] Ljubavin: Jour. Chem. Soc., **58,** 685 (1890); Lottermoser: Zeit. phys. Chem., **60,** 462 (1907); Ber. deutsch. chem. Ges., **41,** 3976 (1908); Zeit. Elektrochemie, **17,** 317 (1911); Fischer: Zeit. Kolloidchemie, **8,** 292 (1911).

[2] Die Bodenkolloide, 20 (1915).

silver nitrate, precipitates when the suspension becomes electrically neutral, stays in suspension as a negatively charged colloid when there is a slight excess of potassium bromide, and precipitates when there is a distinct excess of potassium bromide. At the two ends of this series there is also the possibility of true solution of silver bromide in silver nitrate or potassium bromide.

An interesting case of the precipitation of a colloid by an electrolyte is to be found in the action of sea-water on muddy river water. Skey[1] pointed out that suspended mud is precipitated by electrolytes, and Waldie[2] has discussed the clearing of the water of the Hooghly. When a river flows into the ocean, the current becomes less and some of the suspended mud is dropped on this account; but this is relatively unimportant in many cases. Schloesing[3] called attention to the fact that the formation of deltas is due primarily to the coagulation of the suspension by the electrolytes in the salt water. Another interesting case of the neutralization of an electrical charge is the precipitation of positively charged colloids by β rays.[4] Frischauer[5] found that β rays increase the agglomeration of sulphur, while Doelter[6] reports they change selenium hydrosol to crystalline selenium. Farmer and Parker[7] report that ultra-violet light coagulates colloidal platinum. This seems to be in line with the action of ultra-violet light in causing metals to emit electrons. It would be interesting to know whether the action is confined to metals or whether ultra-violet light will coagulate any negatively charged sol. Svedberg[8] has prepared colloidal solutions apparently by the disintegrating effect of ultra-violet light; but later experiments[9] indicate that the silver is first oxidized and then

[1] Chem. News, **17,** 160 (1868).

[2] Ibid., **30,** 37 (1874).

[3] Jour. Chem. Soc., **24,** 750 (1871).

[4] Hardy: Jour. Physiology, **29,** 29 (1903); Jorissen and Woudstra: Zeit. Kolloidchemie, **8,** 8 (1910); Höber: Physikalische Chemie der Zelle und Gewebe, 332 (1911); Burton: The Physical Properties of Colloidal Solutions, 172 (1916).

[5] Comptes rendus, **148,** 1251 (1909).

[6] Das Radium und die Farben, 17, 95, 97 (1910).

[7] Jour. Am. Chem. Soc. **35,** 1524 (1913).

[8] Zeit. Kolloidchemie, **6,** 130 (1910); Schulze: Ibid., **15,** 136 (1914).

[9] Nordenson: Kolloidchemische Beihefte, **7,** 110 (1915).

reduced. Young and Pingree[1] have done some work on the action of light on colloidal solutions. There is a very important field here especially with reference to the colors of gems; but nobody has attacked the problem systematically.

2. Sols stabilized by Water.—When we come to colloidal solutions peptized by liquids, the effect of salts is necessarily relatively small. Tannin is peptized by water and by glacial acetic acid. Apparent solubilities for tannin vary from 20–250 parts per hundred of water; but Navassart[2] has shown that tannin is miscible in all proportions with water, alcohol, acetone and glacial acetic acid. The apparent solubility has been due to lack of wetting of the tannin powder by the sol. It is probable also that the tendency to coagulate increases with increasing concentration and the presence of impurities might easily cause agglomeration and precipitation at apparently definite concentrations in each case. Salts have relatively little effect on the stability of tannin sols, though the hydroxides of the heavy metals adsorb tannin strongly, the two precipitating together. Gelatine swells in cold water but is not peptized by it. It is peptized by warm water, the apparent melting-point or maximum gelation temperature of a 10 grams per 100 cc gelatine[3] jelly being 30.0°. Salts in relatively high concentration have an effect, and the anions may be arranged in the following order: sulphate > citrate > tartrate > acetate > chloride > nitrate > bromide > iodide > sulphocyanate > benzoate > salicylate. The first three raise the apparent melting-point while the others lower it. From these data it seems probable that the liquefaction by sodium iodide, for instance, is due to a peptization by iodide ion superposed on the water peptization. Briggs[4] has shown that removing iodide by dialysis causes the gelatine to set again; but we have no trustworthy data which show definite adsorption of iodide by gelatine. Glycerine and sugar behave like sulphates, raising the apparent melting-point, while such non-electrolytes as furfurol, urea, alcohol, resorcinol, hydroquinone, and pyrogallol lower the apparent melting-point. Here again we have empirical observations

[1] Jour. Phys. Chem., **17**, 657 (1912).
[2] Kolloidchemische Beihefte, **5**, 299 (1913).
[3] Smith: Jour. Am. Chem. Soc., **41**, 135 (1919).
[4] Jour. Phys. Chem., **24**, 74 (1920).

and no real knowledge. Formaldehyde hardens gelatine so that it is not peptized by water.

By soaps we usually mean sodium palmitate, stearate, or oleate, or some mixture of these salts. They are peptized by water, dilute solutions showing a rise of boiling-point and concentrated solutions practically none by the usual method, which is in error owing to presence of air. By the dew-point method McBain[1] finds a rise of 0.2° for normal potassium stearate. There is, of course, a certain amount of hydrolysis and it seems probable that a sodium oleate solution contains sodium oleate, oleic acid, and caustic soda, the first two of which are not in solution. The hydroxyl ion is unquestionably adsorbed to some extent by the oleic acid or sodium oleate or by both and it is possible that the caustic soda is adsorbed in concentrated solutions It should be possible to verify this assumption by doing ultra-filtration of soap and analyzing the filtrate. A sufficient addition of sodium salts causes the precipitation of soap and this is made use of in soap manufacture. We do not know to what extent this effect of salt is due to a direct coagulation of the soap by adsorbed ions or to coagulation owing to a decrease in the peptizing action of water. Some unpublished experiments by Clowes seem to indicate that the concentration of sodium ions is an important factor, though Kurzmann[2] finds that equimolecular solutions of potassium carbonate and hydroxide behave alike and not equivalent solutions.

3. Sols stabilized by Non-electrolytes or by a Second Colloid. A colloid which is stabilized by a strongly-adsorbed non-electrolyte such as sugar will behave very much like a water-soluble colloid. There has been relatively little work done on such systems. There are many interesting possibilities, however, when we consider the mutual action of two colloidal solutions.

If we mix colloidal solutions of two substances each of which adsorbs the other, the mutual adsorption will have some effect on the adsorption of the peptizing agent. If it causes a decrease in the adsorption of the peptizing agent, this means a decreasing stability of the colloidal solution and may lead to precipitation over some range of relative concentrations. In case this occurs,

[1] Jour. Am. Chem. Soc., **42,** 432 (1920).

[2] Kolloidchemische Beihefte, **5,** 427 (1914).

we shall have colloidal solutions of decreased stability when either colloid predominates sufficiently, and precipitation for intermediate relative concentrations. The range over which precipitation occurs may be great or small depending on the ease with which the peptizing agent is displaced or neutralized. The most familiar case of such precipitation is when we are dealing with two colloids having opposite electrical charges. This point was studied carefully by Biltz[1] and the general statement is to be found in all the text-books on colloid chemistry. The negatively charged colloids studied by Biltz were platinum, gold, selenium, cadmium sulphide, antimony sulphide, arsenic sulphide, stannic oxide, molybdenum blue (MO_3O_8), tungsten blue (W_2O_3), and vanadium pentoxide. The positive colloids were the oxides of iron, aluminum, chromium, thorium, zirconium, and cerium. Precipitation occurs when each positive colloid is mixed with each negative colloid in proper proportions. Since complete neutralization takes place only when one sol has adsorbed the amount of the sol carrying an equivalent amount of the ion having the opposite charge, it follows that the amount of one sol necessary to precipitate a given amount of another sol will vary with the degree of adsorption. It will therefore be a specific property and not not an additive one. This can be tested experimentally on data by Biltz given in Table XLV.[2]

Alumina is more effective than chromic oxide in precipitating antimony sulphide and much less effective in precipitating arsenic sulphide. The alumina must therefore be adsorbed more by antimony sulphide than chromic oxide, while the reverse must be true for arsenic sulphide. Cerium oxide is less effective than either of these in precipitating the sulphides of antimony and arsenic. The phenomenon is thus specific, varying with the nature of the two colloids. This seems not to have been realized before. In fact Freundlich says definitely[3] that one seems to find approximately the same order regardless of what sol is to be precipitated. This statement is true, but it missed the important thing in the experiments, which was that the order was not always the same.

[1] Ber. deutsch. chem. Ges., **37,** 1095 (1904).
[2] Freundlich: Kapillarchemie, 445 (1909).
[3] Freundlich: Kapillarchemie, 445 (1909).

So-called irregular series[1] have been observed when a suspension of a positively-charged colloid is added to a suspension of a negatively-charged colloid. When increasing concentrations of aluminum sulphate were added to a negatively-charged solution of mastic, there was at first no precipitation and the suspension was charged negatively because the mastic was present in excess. At higher concentrations of aluminum sulphate, the suspension became electrically neutral and complete precipitation took place. At still higher concentrations the mastic was held in suspension by the hydrolyzed alumina and the suspension was charged posi-

TABLE XLV.—PRECIPITATION OF NEGATIVE COLLOIDS

		1.4 mg gold completely precipitated by			
CeO_2	Fe_2O_3	ThO_2	ZrO_2	Cr_2O_3	Al_2O_3
4	3	2.5	1.6	0.3	0.1–0.2 mg
		28 mg Sb_2S_3 completely precipitated by			
Fe_2O_3	ThO_2	CeO_2	ZrO_2	Cr_2O_3	Al_2O_3
32	20	11	6.5	3.0	2.0 mg
		24 mg As_2S_3 completely precipitated by			
Fe_2O_3	ThO_2	CeO_2	ZrO_2	Al_2O_3	Cr_2O_3
13	6	4	2	2	0.5 mg

tively. At still higher concentrations of aluminum sulphate, complete precipitation occurred. This apparently abnormal result is due to the fact that the experiment is not exactly what it purports to be, the addition of one colloidal solution to another. Instead of adding a colloidal solution of alumina, there was added a so-called solution of aluminum sulphate, which hydrolyzed to colloidal alumina and sulphuric acid, with possibly some aluminum sulphate left unchanged especially in the higher concentrations. The amount of free sulphuric acid is always equivalent to the amount of alumina and the two concentrations increase proportionally. The so-called abnormal precipitation at the higher concentrations is merely a precipitation by sulphate ions and is absolutely normal.

Since a colloid peptized by water may be charged positively or negatively, there is no reason why it should not precipitate another colloid under suitable conditions. We usually consider the col-

[1] NEISSER and FRIEDEMANN: Zeit. angew. Chem., **1906,** 1953; BECHHOLD: Zeit. phys. Chem., **48,** 285 (1904); BUXTON and TEAGUE: Ibid., **57,** 47, 64 (1907); FREUNDLICH: Kapillarchemie, 402 (1909).

loids peptized by water solely as protecting colloids but this is clearly an inadequate view as is shown by the experimental data. Years ago Schulze[1] pointed out that small amounts of a gelatine solution were as effective as lime or alum in causing the rapid sedimentation of clay and that addition of minute quantities of gelatine to barium sulphate simplified the question of filtration and washing very much. He of course gave no adequate explanation of the phenomenon and the real explanation was given by Billitzer[2] who called attention to the fact that while gelatine, agar-agar, etc., ordinarily check the precipitation of colloidal solutions by electrolytes, small amounts of these same substances may have a precipitating action. This can be detected even when the gelatine produces no precipitation itself. Billitzer cites the experiments of Neisser and Friedemann in which it was found that a mastic emulsion containing a trace of gelatine was precipitated more readily by sodium chloride than when no gelatine is present. Billitzer finds that gelatine precipitates such negative colloids as antimony sulphide and arsenic sulphide in acid or neutral solution, but does not precipitate positively charged sols such as hydrous ferric oxide. Gelatine in ammoniacal solution precipitates hydrous ferric oxide, though no precipitation occurs if ammonia is added to a mixture of gelatine and ferric oxide. Bismarck brown, which is a positive colloid, is precipitated by an alkaline gelatine solution, while eosine is precipitated by an acidified gelatine solution.

Graham[3] points out that colloidal silica is precipitated by gelatine, the composition of the precipitate varying between 56 and 92 parts of gelatine per hundred of silicic acid.

Lumière and Seyewetz[4] have studied the action of salts of chromium upon gelatine because of its importance for the theory of chrome tanning. If a suitable amount of chrome alum is added to a gelatine sol or if sheets of gelatine are soaked long enough in a chrome alum solution, the gelatine becomes insoluble even in boiling water and does not putrefy on standing as the original gelatine would have done. They found first that gela-

[1] Pogg. Ann., **129,** 369 (1866).
[2] Zeit. phys. Chem., **51,** 145 (1905).
[3] Jour. Chem. Soc., **15,** 246 (1862).
[4] Bull. Soc. chim. Paris, (3) **29,** 1077 (1903).

tine could be rendered insoluble by treatment with almost any salt of the formula Cr_2X_6: sulphate, sulphite, nitrate, chloride, fluoride, acetate, formate, citrate, or lactate. Since it had been shown by Namias that the power of chrome alum to make gelatine insoluble was increased by addition of alkali up to the point where precipitation of hydrous chromic oxide occurred, experiments were made with the green basic chromic sulphate of Recoura. Gelatine treated with a solution of this salt resisted repeated washing with boiling water better than gelatine which had been treated with a solution which was not basic. On the other hand, gelatine is not made insoluble by treatment with a so-called solution of chromic oxide in potassium hydroxide; but this is probably due to the excess of alkali. If the proper amount of ammonia is added to gelatine and then a chrome alum solution, the gelatine becomes insoluble in boiling water; but this is not the case if ammonia is present in excess. The gelatine is insoluble when it contains 2.5–25 grams of chrome alum per hundred of gelatine.

Experiments with chromic sulphate, chloride, nitrate, and acetate showed that approximately the same quantity of chromic oxide was necessary to make the gelatine insoluble irrespective of the nature of the acid. Since this implies that only the chromic oxide counts, experiments were made to see what became of the acid radical. Sheets of gelatine were immersed in a known chromic sulphate solution and the solution analyzed afterwards. The ratio of chromium to sulphate in the solution was practically the same before and after treatment with gelatine, which meant apparently that the chromic sulphate was taken up as a whole. It could not be the chromic sulphate as such which made the gelatine insoluble because the same result could be obtained when chrome alum was added to an ammoniacal gelatine. When the gelatine containing chromic sulphate is washed repeatedly with boiling water, acid is extracted very slowly; but after some washings the gelatine swells and a little is carried off in the wash water, leaving the residue relatively richer in chromium, the chromic oxide content running up to 5.4–4.6 grams per hundred grams of gelatine. If the gelatine is treated with dilute alkali, it is possible to remove the acid without causing any swelling or any solution of the gelatine. When the gelatine is treated

in this way the maximum amount of chromium found in the gelatine is 3.3–3.5 grams Cr_2O_3 per hundred grams of gelatine.

The explanation seems to be that the chromic oxide makes the gelatine insoluble and that the acid is adsorbed strongly by the chromic oxide, the gelatine, or both. When the acid is washed out at high temperatures, it causes a swelling of the gelatine. In fact, an insoluble gelatine, which has been freed from acid, swells rapidly and finally dissolves if boiled with water containing small amounts of acid or alkali. If the acid is adsorbed by the chromic oxide in the gelatine, it would be interesting to know whether there is a time factor and whether after standing for a month it would be easier to wash out the acid.

Coming back to the general problem, if the ratio of gelatine to the other colloid is increased sufficiently, we shall pass through the precipitation range into the range where the colloidal solution is stabilized by gelatine and then behaves more like a water-soluble colloid. Colloidal gold and colloidal silver solutions, when stabilized by gelatine can be evaporated and redissolved because the gelatine prevents the irreversible agglomeration. When less gelatine is used, it may retard, though not prevent, the change of red colloidal gold to blue. Zsigmondy[1] defines as the gold number the number of milligrams of a protecting colloid which just prevents the color change in a 10 cc red gold solution, containing 0.0053–0.0058 percent gold, when one cubic centimeter of a ten percent sodium chloride solution is added. Of course a strongly adsorbed non-electrolyte, such as sugar, will act similarly to gelatine; but, in most cases, the adsorption is so much less that these substances are only interesting theoretically as stabilizers. Some of his results are given in Table XLVI.

Most of the stable colloidal solutions depend for their stability on the presence of a so-called protecting colloid. There are several other ways in which this property can be made useful. If we have colloids like the so-called zinc and magnesium resinates which are peptized by benzene, we can use these as protecting colloids to stabilize pigments and thus form colloidal solutions which could not otherwise exist in benzene. There are other cases where one does not insist on a colloidal solution but wishes a fine-grained precipitate. The most important case of this sort

[1] Zeit. anal. Chem., **40**, 697 (1901).

technically is the photographic emulsion, which consists chiefly of silver bromide precipitated in presence of gelatine, so as to get a fine-grained precipitate, which is afterwards given the desired properties by agglomerating through suitable treatment. The gelatine plays the additional part of a depolarizer.

TABLE XLVI.—GOLD NUMBER FOR DIFFERENT COLLOIDS

Colloid	Gold number
Gelatine	0.005–0.01
Caseine	0.01
Egg albumin	0.06–0.3
Gum arabic	0.15–0.25
Gum tragacanth	2
Dextrin	10–20
Potato starch	25
Sodium oleate	0.4–1.0
Sodium stearate (added boiling hot)	0.001
Sodium stearate (added at 60°)	10

Even though the gelatine or similar substance may not be present in sufficient amount to prevent precipitation, its presence may make itself known by cutting down the agglomeration of the colloidal precipitate. When caseine is precipitated from cow's milk by acid, it comes down in relatively coarse lumps which is one reason why cow's milk is bad for infants. By adding gelatine[1] to the milk, the growth of the curdy precipitate can be prevented. In human milk a protecting colloid is present and consequently coarse curds are not formed. This property of gelatine and other strongly adsorbed substances of keeping down the size of precipitates is made use of in the preparation of many colloidal solutions. By varying the amount of gelatine one can vary the fineness of the precipitate. The addition of gelatine to ice cream prevents the formation of coarse crystals. In electrolytic refining of metals and in electroplating, addition agents are used to make the deposited metal less coarsely crystalline. An addition agent must not be carried away from the cathode by the current and must be adsorbed by the precipitating metal.

[1] ALEXANDER: Jour. Soc. Chem. Ind., **28**, 280 (1909).

Gelatine is used in lead refining and has a great effect in an acidified copper sulphate solution. Many of the essential oils have proved satisfactory. Glucose can also be used in some cases, not because it is a colloid, but because it is adsorbed strongly by the precipitating metal.

In the case of two colloids, each peptized by water, the mutual adsorption may cut down the adsorption of water sufficiently to cause precipitation. This seems to be the most plausible explanation for the behavior of gelatine and tannin. The only difficulty is that the adsorption is more marked when the gelatine is positive and the tannin negative, which is more what one would expect if the two were colloids peptized by ions. There seem to be at least two possible ways out of this difficulty. It may be that gelatine is not really peptized by water[1] and that we are dealing with a case of ion peptization where the range of instability is very small. The other possibility is that we get a different adsorption when the colloids are charged oppositely and that the resulting complex is less readily peptized by water under those conditions. This is not an impossibility, as is shown by the fact, previously mentioned, that ammoniacal gelatine precipitates colloidal ferric oxide, whereas there is no precipitation if the gelatine and ferric oxide sols are mixed before the ammonia is added. There seems to be no way at present to decide this question.

Tannin and basic dyes give a precipitate but the range over which this occurs is very limited and in order to make use of this property in dyeing, it is customary to fix the tannin with a salt of antimony. Of course, in so far as the water peptization is cut down, the mixture will tend more and more to behave like a colloid peptized by ions.

Tiebackx[2] finds that when a half percent gelatine solution is mixed with a four percent gum arabic solution, the mixture is precipitated readily by acids. If the acid is washed out, the coagulum can readily be dispersed in water. Tiebackx points out that the properties of a gelatine and gum arabic mixture are almost those of a globulin or of caseine. "Caseine is peptized by dilute alkalies and somewhat stronger acids, the precipitation

[1] Cf. Loeb: Jour. Gen. Physiology, **1**, 365 (1919).

[2] Zeit. Kolloidchemie, **8**, 198, 238 (1911).

range lying between these two limits. Sulphuric acid is also adsorbed by caseine somewhat more strongly than hydrochloric acid. With globulin and caseine the acids are also displaced by salts as can be shown by means of methyl orange. The displacement of acid also involves a peptization, for van Dam[1] has shown that presence of five percent sodium chloride increases the amount of caseine peptized by a given concentration of acid."

Apparently gelatine and agar-agar are two practically non-miscible liquids, for Beijerinck[2] reports that it is impossible to mix a hot ten percent gelatine solution with a hot two percent agar solution, one of the liquids being emulsified in the other when the two are shaken together. The phenomenon is even more marked when ten percent soluble starch is shaken with ten percent gelatine.

Biltz[3] obtained no precipitation upon mixing any two of his positively charged sols and no precipitation on mixing any two of the negatively-charged sols except when gold or selenium was mixed with the sulphides and then chemical action probably took place. Biltz concluded that sols of like charge had no effect upon each other; but this does not follow, because adsorption of one colloid by the other would not neutralize the electrical charge and therefore would not cause precipitation. We know, however, that cases of adsorption are not limited to colloids or electrolytes having opposite signs. Charcoal adsorbs both bases and acids. Silver bromide adsorbs silver ions or bromine ions as the case may be. There is therefore no theoretical reason why precipitated hydrous ferric oxide might not adsorb chromic oxide and vice-versa. If the precipitated substance will do this there is no reason why the peptized substance should not. Nagel[4] has shown recently that this does occur and that it accounts for the behavior of mixtures of chromic and ferric salts with excess of alkali. Hydrous chromic oxide is peptized by caustic potash while hydrous ferric oxide is not. If the chromium salt is present in large amount relatively to the iron salt, the ferric oxide will adsorb the peptized chromic oxide and be pep-

[1] Van Bemmelen Gedenkboek, 104 (1910).
[2] Zeit. Kolloidchemie, **7**, 16 (1910).
[3] Ber. deutsch. chem. Ges., **37**, 1095 (1904).
[4] Jour. Phys. Chem., **19**, 331 (1915).

tized by it, going apparently into solution. If the ferric salt is present in excess, it will adsorb the peptized chromic oxide, carrying it out of the liquid phase. It is to be noticed that the chromic oxide, when in excess, acts as a so-called protecting colloid to the iron oxide. Other cases of the same type could be cited. The fact that gelatine protects ferric oxide when added before the ammonia shows that it must have been adsorbed by the ferric oxide. Bechhold[1] has shown that an ultra-filter which will stop Prussian blue and will let arsenic sulphide pass, holds back the arsenic sulphide when mixed with Prussian blue. Although both are negatively charged sols, it seems evident that there is a mutual adsorption. On the other hand, Bechhold found that hemoglobin can be separated from Prussian blue by filtration through a suitable ultra-filter, the hemoglobin going through the filter. In this case there is no appreciable adsorption.

Since the precipitation of one colloid by another may take place within a relatively narrow range of concentrations, it is not surprising that people have postulated the existence of definite chemical compounds in order to account for the precipitation. The literature on this subject is in a worse state even than that on the so-called basic salts. To cite a few cases out of many, ferric arsenate, aluminum silicate, aluminum stannate, stannic phosphate, and cupric eosinate are not formed under ordinary conditions by precipitation from solution. The precipitation is due to the mutual coagulation of two colloids. If each adsorbs the other pretty strongly, it may easily happen that the precipitate can be peptized without change of composition under certain conditions, a behavior which one usually associates with compounds. The color lakes are an especially fruitful field for imaginary formulas. Unpublished work by Mr. Basseches of the Bureau of Standards shows that no ferric tannate is formed under ordinary conditions.

The purple of Cassius is a typical case. It is usually prepared by the reaction of gold chloride with stannous chloride and consists of colloidal gold adsorbed by stannic oxide. Since it could apparently be carried into solution by ammonia and since mercury did not extract gold from it, Berzelius was positive that it must be a compound and he wrote for it the formula, $Au_2O_2.Sn_2O_3$.

[1] Zeit. phys. Chem. **60**, 299 (1907).

xH_2O. The final proof that it was a colloidal precipitate was given by Zsigmondy[1] who made it directly from colloidal gold and colloidal stannic oxide. Owing to the intensity of the color, the formation of the purple of Cassius may be used as a test for gold,[2] sensitive to one part in one hundred million. It has also been possible to obtain similar precipitates with alumina, barium sulphate, mercurous chloride, etc.[3] A corresponding brown[4] and red[5] precipitate has been obtained with platinum. When purple of Cassius is made with zirconia, the precipitate is not peptized by ammonia and aqua regia does not extract the gold.[6]

[1] Liebig's Ann., **301,** 375 (1898).

[2] Rose: Jour. Chem. Soc., **64** II, 245 (1893).

[3] Schwarz: Jour. Chem., **26,** 205 (1873); Müller: Ibid., **48,** 352 (1885); Krüss: Ibid,. **52,** 16 (1887); Antony and Lucchesi: Ibid., **72** II, 43 (1897); Marshall and Welker: Jour. Am. Chem. Soc., **35,** 822, 823 (1913).

[4] Delachanal and Mermet: Comptes rendus, **81,** 370 (1875).

[5] Wöhler: Zeit. Elektrochemie, **14,** 634 (1908).

[6] Biltz: Ber. deutsch. chem. Ges., **37,** 1095 (1904).

CHAPTER VIII

GELATINOUS PRECIPITATES AND JELLIES

Structure

When we add caustic soda to a ferric chloride or an aluminum chloride solution, we get a precipitate which varies from gelatinous to sandy, depending on the temperature, being more sandy the higher the temperature of precipitation. In this case we have the gelatinous precipitate and a supernatant liquid. If we add caustic potash in excess to a chromic sulphate solution, we may get a gelatinous precipitate with a supernatant liquid or we may get the whole mass setting to a jelly, which may afterwards contract and squeeze out liquid.[1] To avoid confusion in the future it will be simpler to use the word jelly only for those cases where there is no supernatant liquid at first. This is in accord with general usage for one speaks of a gelatine solution, for instance, setting to a jelly; but some writers have been so careless in their use of the word that it has not always been clear just what they did mean. Gel is the inclusive term, gelatinous precipitates and jellies being two forms of gels.

A gelatinous precipitate is always viscous and contains liquid; it may be plastic. No one has any difficulty in recognizing a gelatinous precipitate; but we are not at all clear as to what gives it these physical properties. In the case of gelatinous ferric oxide there is every reason to suppose that none of the water is combined to form a definite chemical compound. Vapor pressure experiments on silicic acid jellies show no evidence of any definite chemical compound between silica and water. Le Chatelier[2] believes that a silicic acid jelly is merely grains of anhydrous silica and water. He claims to have proved this by polishing metals with colloidal silicic acid; but this is not conclusive because anhydrous silica might have been formed as a result of the

[1] Syneresis is the technical term.

[2] La Silice et les Silicates, 76 (1914).

pressure used in polishing. A better line of attack is to consider whether grains of sand mixed with water could give a precipitate having the properties of gelatinous silicic acid. Presence of water will make sand plastic, and addition of an excess of water will give a mass of wet sand with supernatant liquid, which is good so far as it goes. If the sand is shaken with an excess of water, the grains will be separated and will afterwards settle at a given rate depending on the conditions. That does not happen with the silicic acid jelly. There is a marked coalescence which we do not get with sand and water so far as we know. We must therefore assume one of two things. Either the sand grains are held together extraordinarily firmly by water when they are very fine or there is some other factor comes in. The first explanation cannot be the right one because, if it were, one ought then to be able to get a gelatinous precipitate of any colloid at ordinary temperatures without much difficulty, which is not the case. We never get gelatinous gold and while we can get gelatinous calcium carbonate, we have to do it in a very special way. Consequently, Le Chatelier's hypothesis cannot be accepted without modification. We are not dealing with a solid solution because then the vapor pressure would be independent of the previous history of the sample.

It seems to me that Odén's experiments on sulphur are very important in their bearing on this problem. Odén[1] found that the physical properties of sulphur precipitated from colloidal solution varied very markedly with the electrolyte used for precipitation. It came down as a hard precipitate with potassium salts, fine-grained with copper sulphate, plastic with barium salts, fluid with hydrochloric acid, and slimy with other salts. Similar but less marked phenomena have been observed with colloidal ferric oxide,[2] which comes down more sandy when precipitated by hydrochloric acid than when precipitated by sulphuric acid.[3] In the case of sulphur we are not very far below the melting-point and we know that it is a simple matter to supercool molten sulphur so as to get a plastic mass at ordinary

[1] Der kolloide Schwefel, 134, 157 (1912).

[2] Giolitti: Gazz. chim. ital., **35** II, 181 (1905); **36** II, 157, 433 (1906).

[3] For alumina with chlorides and sulphates see Rose: Zeit. Kolloidchemie, **15,** 1 (1914).

temperatures. The simplest assumption is that the sulphur precipitated from colloidal solution may contain enough water and electrolytes to keep it as a supercooled viscous liquid the drops of which have coalesced presumably to form filaments or perhaps nets, thus giving it a structure. The only apparent difference between the sulphur and the ferric oxide is that we never get as fluid a mass with the iron oxide as with the sulphur; but that may be due to the difference in the melting-points. It seems possible therefore that a gelatinous precipitate consists of partially coalescing drops or films of a viscous liquid containing more or less of the mobile liquid adsorbed or held in other ways. The super-cooled liquid is kept from solidifying by the water or the electrolyte or both. While this does not seem a very satisfactory hypothesis, it is not an impossible one. With benzoic acid and water we get two liquid phases which are stable. With salicylic acid and water the two liquid phases are instable but can be realized without any difficulty. On this basis rapid precipitation would be likely to get us down to the instable curve for the dineric system and that is exactly what happens. Von Weimarn[1] obtains any anhydrous inorganic salt as a gelatinous mass by precipitating under such conditions that the percentage supersaturation is enormous. It is also interesting to note that gelatinous precipitates are obtained only as a result of condensation methods. Where the reverse seems to be the case, as in the peptization of silica, it is probable that true solution occurs, followed by precipitation. There is no doubt but that silicic acid can exist temporarily in true solution. Mylius and Groschuff[2] showed that when a sodium silicate solution was acidified with hydrochloric acid, the silicic acid set free diffused fairly readily and lowered the freezing-point. These two characteristics disappeared gradually as the free acid changed into colloidal silica.

If one objects to the distinctly arbitrary assumption that we have viscous liquids and water in the gelatinous precipitates, one alternative is to assume that solid particles and water behave like a gelatinous precipitate when the solid particles are sufficiently fine and provided they adsorb water sufficiently strongly.

[1] Grundzüge der Dispersoidchemie, 67 (1914).

[2] Ber. deutsch. chem. Ges., **38**, 116 (1905).

This is apparently what Zsigmondy[1] does; but he does not show why this should be so. Another alternative is to assume that the adsorbed ion makes the surface viscous. In the case of an emulsion this does happen. We may have drops of oil coated with a soap film and these may coalesce sufficiently to form a gelatinous mass. This is not helpful because the soap is gelatinous in itself. It is possible, however, that there is an intermediate stage between that of peptization and that of irreversible coagulation, where there may be a surface which is gelatinous in its properties. While something of this sort may happen, it has not been shown to take place. The real test would be to make a gelatinous gold precipitate without any protecting colloid. Until something of this sort has been done, or until we know why it cannot be done,[2] we must admit that we know very little in regard to what constitutes a gelatinous precipitate. A possible explanation with ferric oxide is that we have grains of oxide with a gelatinous film of instable ferric hydroxide adsorbed on the surface and stabilized thereby. This would not be inconsistent with the vapor pressure data because those only show that ferric hydroxide does not exist in mass under the conditions of the experiment. We know that sand can be converted into gelatinous silicic acid if ground sufficiently fine and that clay particles have a gelatinous coating. The difficulty is that this explanation does not help us in the case of barium sulphate and we must either explain all gelatinous precipitates in the same way or we must divide them into groups and be able to distinguish between the groups.

We do not know for certain what the structure of a gelatinous precipitate is. We may have viscous drops coalescing partly to form filaments or films, or we may have spherical drops of water coated with the gelatinous material. This second case is really water emulsified in water, which seems improbable; but a mass of foam is air emulsified in air, so that such a system is not impossible. This would constitute a honeycomb structure whereas the other type gives the interlacing or sponge structure, each phase being continuous. The general opinion at present

[1] Kolloidchemie, 149 (1912).

[2] It has been suggested that gold does not adsorb water sufficiently strongly to give a gelatinous precipitate.

is that gelatinous precipitates and jellies have a sponge structure.[1] On the other hand we know that certain emulsion jellies have the honeycomb structure. The fact that one can do ultra-filtration through a suitable gelatine or collodion membrane is a strong argument in favor of a porous structure in these particular cases. On the other hand, a collodion membrane can be made which is less permeable to air and more permeable to hemoglobin than the collodion ultra-filter,[2] thus indicating an entirely different structure.

We can now consider the structure of jellies. It seems probable that in a jelly we have the concentration of the more viscous constituent equal to or greater than that necessary to give zero fluidity. It has already been shown that certain graphite powders give zero fluidity at a concentration of 5.5 percent graphite and that this could be accounted for if the thickness of the adsorbed film were a little greater than the radius of the graphite particle. If there is partial agglomeration to larger masses, the viscosity will increase and zero fluidity can be reached at lower concentrations for the same relative thickness of adsorbed film or at the same concentration with a lesser relative thickness of adsorbed film. If the particles coalesce partially to form something analogous to a string of beads or if they form threads, the viscosity will be increased very much and jellies can be obtained at very low concentrations. All these things have been observed. Bachmann[3] has shown that when soap solutions set to a jelly, long threads are formed. In the case of sodium stearate a translucent jelly can be obtained containing less than one percent sodium stearate. These threads undoubtedly go over finally to a net structure.

With starch and water Meyer[4] has observed the formation of a net structure made up distinctly of drops or globules. In cases where there is a structure without the visible globules being in apparent contact, it is probable that the larger ones are ce-

[1] Quincke: Drude's Ann., **10,** 482 (1903); **14,** 489 (1904); Zsigmondy: Zeit. anorg. Chem., **71,** 356 (1911); Bachmann: Ibid., **73,** 125 (1912); Flade: Ibid., **82,** 173 (1913).

[2] Bechhold: Zeit. phys. Chem., **64,** 337 (1903).

[3] Zeit. Kolloidchemie, **11,** 145 (1912).

[4] Kolloidchemische Beihefte, **5,** 1 (1913).

mented together by smaller ones which are invisible under the conditions of the experiment. It is interesting to note that the single drops are never homogeneous but are always turbid. With gelatine in aqueous alcohol it is possible to get a net structure made up of globules rather than filaments. Meyer considers that all the starch-water jellies are porous masses with both phases continuous. Hardy[1] believed that concentrated gelatine jellies consisted of drops of water suspended in a gelatine-rich phase; but this conclusion was based on the result of compressing jellies and consequently needs further confirmation.

It seems probable that the concentrated gelatine jellies with drops of water suspended in a gelatine-rich phase should not be considered to have a honeycomb structure in the sense that an emulsion has a honeycomb structure. With the emulsion there is a film of a third substance around the dispersed drops and we should still have an emulsion if the outer phase could suddenly be made fluid. Under similar conditions the drops of water in a gelatine jelly would undoubtedly run together. A gelatine jelly of the type under consideration is merely a viscous medium in which water is dispersed. If we knead water into butter we do not get a true emulsion any more than we get a true froth when we knead air into dough or into soap. In the case of emulsions the type depends on the nature of the third substance and not on the relative masses of the two liquids. If a gelatine-water mixture were the water-in-oil type at any concentration, it would have to be a water-in-oil type at all concentrations. A good deal of stress has been laid at times on the alleged fact that ultramicroscopic examination has shown that jellies have a sponge structure and not a honeycomb structure; but it is at last admitted that we cannot distinguish between these two cases by means of the ultra-microscope.[2]

It has always been assumed tacitly that each so-called phase in a gelatine jelly is truly homogeneous and attempts have been made to determine the composition of one of the phases by squeezing liquid out of a gelatine jelly and analyzing it. Quite apart from errors of manipulation, which are probably large, the underlying assumption is not necessarily sound. If we

[1] Zeit. phys. Chem., **33,** 326 (1900).

[2] Bachmann: Zeit. Kolloidchemie., **23,** 89 (1918).

shake up fairly pure oil with fairly pure water, the mixture separates into two liquid layers, the oil layer containing some dispersed water and the water layer containing some dispersed oil. Since water peptizes gelatine under certain conditions, there is no reason liquid gelatine or a gelatine-rich phase should not peptize water. It is probable therefore that with gelatinous precipitates and with jellies we have a binary system in which each constituent peptizes the other. A necessary characteristic of such a system is that what we ordinarily consider the separate phases will never be homogeneous. The gelatine-rich phase will always contain peptized water and the water-rich phase will always contain peptized gelatine. Theoretically this can be carried on indefinitely because the peptized water may peptize gelatine and the peptized gelatine may peptize water; but practically there will soon come a point beyond which no effect can be detected. The predicted lack of homogeneity in what would ordinarily be a separate phase has been commented on by Meyer[1] in his studies on starch.

A dilute colloidal solution of gelatine in water will consist essentially of turbid drops of a gelatine-rich phase dispersed in water. With increasing concentration of gelatine, there will be a tendency for the separate drops to coalesce into larger drops. If they are too viscous to do this, they may coalesce partially forming threads or, to a still lesser extent, forming a chain of beads. In this latter case it is not necessary that the drops themselves should be in actual contact. In the preliminary stages it may only be the adsorbed films of water which are in contact, just as happens with a plastic mass of sand and water. If the dispersed drops are of different sizes, the smaller drops will probably group themselves around the larger ones, so that the latter will be held in place by a much less visible group of smaller drops.

With increasing concentration of gelatine, loose chains may be formed which will then pass into a net or sponge structure of which a granular jelly is an extreme form. In jellies of this type, both phases are continuous and we are dealing with an interlacing system With still further increase in the gelatine we may get water dispersed as definite drops in the gelatine-rich phase.

[1] Kolloidchemische Beihefte, **5**, 1 (1913).

While this might be called a honeycomb structure, Meyer[1] is probably right in not so classifying it. It is probably better to reserve the term "honeycomb" for structures in which the cell walls are thin relatively to the diameter of the cells and it may be desirable to restrict it to cases like the emulsions where there is a distinct film round the drops.

Owing to our comparative ignorance in regard to jellies, we do not know to what extent increasing the concentration of gelatine, for instance, causes the mass to fill up with chains or filaments of the same diameter or to what extent each filament increases in cross-section. It is the absence of a satisfactory working hypothesis that makes it so difficult to account for many of the properties of jellies.

If a porous jelly of the interlacing type be allowed to dry at constant temperature, the walls may be rigid enough not to collapse completely, in which case we shall eventually get an interlacing system with air in the pores. If the walls are not rigid, they may collapse to such an extent that the pores will disappear practically completely. If the walls do not unite when thus brought in contact, or if there is formed something analogous to a scar, the behavior of the jelly, when placed in water, will vary with its previous history. If the walls coalesce absolutely and uniformly, the rate and amount of swelling will be independent of the previous history of the jelly.

Since a gelatinous precipitate differs from a jelly in that the latter has not contracted and excreted liquid, it follows that we shall get jellies when the conditions for precipitation are such as to avoid marked contraction. With gelatine or agar the tendency to form jellies is so strong that no special precautions are necessary. In most cases, however, a slow precipitation is essential where there is a tendency to form a gelatinous precipitate.[2] A striking instance of this occurs in dialysis where the liquid in the dialyzer is very apt to set to a jelly just before the colloid is entirely pure, in other words just as the peptizing agent is brought slowly below a critical value.[3] Slightly sour milk coagulates on boiling and a very acid milk will set to a solid mass

[1] Kolloidchemische Beihefte, **5**, 30 (1913).

[2] Holmes and Fall: Jour. Am. Chem. Soc., **41**, 763 (1919).

[3] Holmes and Arnold: Jour. Am. Chem. Soc., **40**, 1014 (1918).

at room temperature. This is a case of a gradual production of precipitating agent and therefore fits in with our general point of view. This is not always understood and it is a popular belief in Sweden that the so-called "dicke Milch" cannot be made in winter. All this means is that the kitchens are ordinarily so cold in winter that the lactic acid fermentation does not take place sufficiently rapidly. The same effect can be produced by a suitable addition of acetic acid.[1] A so-called calcium sucrate solution sets to a jelly on addition of carbon dioxide.[2] When caseine is heated with water, the solution becomes more turbid and this turbidity is more marked in presence of calcium salts which tend to precipitate it.[3] With a suitable amount of calcium chloride the liquid clots.[4] Calcium chloride and milk require a higher temperature to cause clotting and calcium chloride does not cause milk to set to a jelly at ordinary temperatures. It is not known what constituent in the milk checks the clotting. There are a number of things about the coagulation of milk by rennin which need further study.

In the case of some inorganic jellies, the presence of certain ions seems to be necessary either to ensure sufficiently slow precipitation or to prevent contraction. To get chromic oxide jellies[5] acetate or sulphate must be present. With cupric oxide jellies[6] a small amount of sulphate is necessary. It is surprising in what a number of cases it is possible to get inorganic jellies. Delafontaine[7] found that jellies are formed when ammonia is added to yttrium, didymium, lanthanum, and erbium acetates. Ferric oxide, glycerine and alkali form a jelly on dialysis which liquefies on adding alkali.[8] Zinc oxide[9] and mercuric oxide[10]

[1] Loevenhart: Zeit. phys. Chem., **41,** 189 (1904).

[2] Horsin-Deon: Jour. Chem. Soc., **26,** 612 (1872).

[3] Van Slyke and Hart: Am. Chem. Jour., **33,** 467 (1905).

[4] Ringer: Jour. Physiology, **11,** 470 (1890).

[5] Bunce and Finch: Jour. Phys. Chem., **17,** 269 (1913); Nagel: Ibid., **19,** 331 (1915).

[6] Finch: Jour. Phys. Chem., **18,** 26 (1914).

[7] Chem. News, **73,** 284 (1896).

[8] Grimaux: Comptes rendus, **98,** 1485, 1540 (1884); Fischer: Biochem. Zeit., **27,** 223 (1910).

[9] Kuriloff: Zeit. Elektrochemie, **12,** 213 (1906).

[10] Bunce: Jour. Phys. Chem., **18,** 269 (1914).

jellies have been made. Klemp and Gyrlai[1] discuss the formation of arsenate jellies. Crum[2] made an alumina jelly containing 1/600 alumina and 1/7500 sulphuric acid. Bentley and Rose[3] dissolve hydrous alumina in 8 percent acetic acid and add acetic acid. Pickering[4] states that basic aluminum sulphate can be obtained either flocculent or as a jelly. It is a little difficult to see how a jelly containing 1/600 alumina and 1/7500 sulphuric acid can possibly be solid if it has a sponge or net structure, whereas there would be no difficulty in case there was a honeycomb structure. It is also not clear how coagulation to a net structure can give a gel without any supernatant liquid. There is a good deal more careful work to be done on jellies before we can be sure of what happens in each particular case. With one percent sodium stearate jellies, it seems to be certain that the particles agglomerate to form filaments.[5]

Vapor Pressure Relations

If the inorganic jellies are not hydrated we should expect the vapor pressure concentration curve to be similar in type with that of charcoal and water, a smooth curve with no breaks. This is what happens with the exception that the pores in the jellies may change in size, in which case the curve will not be reversible.

Over fifty years ago, Davies[6] showed that hydrous ferric oxide could be dehydrated completely by prolonged heating under water, which of course could not be the case if a definite hydrate were formed; but is just what might be expected if the ferric oxide changed in structure and became less adsorbent. Over forty years ago Ramsay[7] showed that the rate at which hydrous ferric oxide lost water was not constant and that consequently there could be no definite hydrate within the range studied. Twenty

[1] Zeit. Kolloidchemie, **15,** 202 (1914).

[2] Jour. Chem. Soc., **6,** 216 (1854).

[3] Jour. Am. Chem. Soc., **35,** 1490 (1913); Rose: Zeit. Kolloidchemie, **15,** 1 (1914).

[4] Jour. Chem. Soc., **42,** 700 (1882).

[5] Bachmann: Zeit. Kolloidchemie, **11,** 145 (1912).

[6] Jour. Chem. Soc., **19,** 71 (1865).

[7] Ibid., **32,** 395 (1877).

years ago van Bemmelen[1] determined the isotherm for ferric oxide and water, finding no indication of a definite compound. On the other hand, a definite compound, $Fe_2O_3.H_2O$, is found in nature as the minerals, Göthite and Lepidocrite.[2] This can be made in the laboratory by decomposing sodium ferrite, Na_2FeO_4, but in no other way. This hydrate behaves on dehydration exactly as a definite compound should. The vapor pressure of the hydrous ferric oxide changes with the time and therefore depends on the previous history of the sample.

There is no evidence of any hydrate of chromic oxide[3] between 15° and 28°. The case of hydrous cupric oxide is a little more difficult because the vapor pressure becomes practically zero at the composition, $CuO.H_2O$, and consequently one cannot tell from pressure measurements whether a definite compound occurs or not. If a definite compound existed with a practically zero pressure, it should form from cupric oxide in presence of water. Actually the reverse thing happens and the blue gelatinous cupric oxide goes over spontaneously into the black cupric oxide under water. This change can be prevented by the presence of hydrous oxides of nickel, cobalt, chromium, aluminum, mercury, magnesium, zinc, or manganese.[4] Consequently we conclude that no definite hydrate is formed under ordinary conditions. This does not exclude the possibility of a definite hydrate[5] being formed under special conditions.

While these experiments show that some cherished hydroxides do not exist, there are others which stand the test. Van Bemmelen recognizes the existence of $BeO.H_2O$, $MgO.H_2O$, $MnO.H_2O$, and $Al_2O_3.3H_2O$. It is not clear why $Al_2O_3.3H_2O$ should be a definite compound and $Fe_2O_3.3H_2O$ and $Cr_2O_3.3H_2O$ not; but that seems to be the case.

The case of silicic acid has been studied with great care by van Bemmelen.[6] A dilute jelly may contain about 300 mols of water to one of silica. Such a jelly flows together again when

[1] Zeit. anorg. Chem., **20,** 185 (1899).
[2] Posnjak and Merwin: Am. Jour. Sci. (4), **47,** 311 (1919).
[3] Van Bemmelen: Die Absorption, 78 (1910).
[4] Blucher and Farnau: Jour. Phys. Chem., **18,** 629 (1914).
[5] Bonsdorff: Zeit. anorg. Chem., **41,** 134 (1904).
[6] Die Absorption, 196, 214, 232 (1910).

broken into pieces. When the water content is only 30–40 mols the gel can be cut and will stand alone. With 20 mols the gel is stiff, and it is brittle when the content is 10 mols. At 6 mols the gel can be pulverized and the powder is apparently dry. The vapor pressure is practically that of pure water down to a water content of 6 mols per mol of silica. On further dehydration the vapor pressure curve drops continuously with no sign of the existence of any definite compound. When the water content drops to somewhere usually between 1.5 and 3.0 mols with different samples, the gel becomes opaque and chalky but clears up again when the water content reaches about 0.5–1.0 mols. The cloudiness begins when the first air bubbles appear in the pores and lasts until the pores are filled completely with air. Owing to the action of capillarity the water which evaporates from the outer surface of the capillaries is at once replaced from the inside of the gel, leaving a vapor space in the centre of the jelly. This produces an opacity which lasts until the pores are free from capillary water. The balance of the water 0.5 –1.0 mol is probably adsorbed so strongly on the surface of the capillaries that it is almost impossible to remove it, just as we have already seen that heating charcoal 100° above the boiling-point of benzene does not necessarily remove the last traces of benzene. As the water passes off, the volume of the gel shrinks until the clouding begins, after which there is practically no change in volume during further loss of water. This is shown by the data in Table XLVII.

TABLE XLVII.—VOLUMES OF SILICA JELLIES

Mols H_2O per mol SiO_2	Volume	Mols H_2O per mol SiO_2	Volume	Mols H_2O per mol SiO_2	Volume
122.0	29	11.3	3.0	clouding	
75.7	18	2.8	1.0	1.0	0.73
45.2	11	2.2	0.86	0.39	0.73
23.2	4	1.7	0.75	0.3	0.73

In Fig. 10 is given a schematic representation of the pressure-concentration relations at 15° for a freshly prepared silica gel.

The A-curves represent the first dehydration over sulphuric acid. The Z-curves are for material which has been dehydrated once more or less completely. The direction of the arrows shows whether dehydration is taking place. Starting with a freshly prepared gel, the vapor pressure drops below that for pure water and the dehydration curve consists of the three portions $A\beta$, $A\alpha\beta$ and $A\alpha$. There is probably an actual break in the curve at O, where the gel begins to cloud and it is doubtful whether there is a break at O_1 where the clouding ends. Owing to the decrease in volume as far as O, the capillaries are entirely filled with water and the gel is transparent. Since the volume does not change much after reaching O, the capillaries necessarily

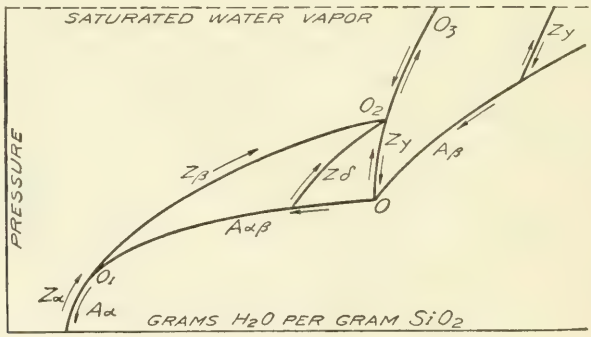


Fig. 10.

begin to fill with air as the water evaporates and the gel becomes turbid even up to the point of chalkiness. Owing to capillary action the liquid is always drawn to the outer surface of the capillaries and the clouding starts at the center. By the time O_1 is reached the capillaries are full of air except for a layer of strongly adsorbed water and the gel becomes clear again. Along the curve $A\alpha$ the last traces of adsorbed water are driven off. If the dehydration is stopped at some point on $A\beta$ and if the gel is exposed to higher partial pressure of water vapor, it is found that the hydration is not reversible and we get a curve $Z\gamma$. While the gel shrinks along $A\beta$, it does not swell again to any appreciable extent and consequently it does not take up water under the same conditions. The curve $Z\gamma$ repre-

sents reversible phenomena at least until the dehydration has been carried beyond the point where $Z\gamma$ meets $A\beta$. From O to O_1 we have an irreversible pressure change. If the dehydration is stopped at any point we get curves for hydration like $Z\beta$ and $Z\delta$ which usually meet as drawn in the point O_2. From O_2 to O_3 the pressure-concentration curve is reversible. From O_2 we pass to O on dehydration. It is possible to pass along the path OO_1O_2O as often as one likes but only in the one direction. The loop OO_1O_2O is therefore a hysteresis loop. Zsigmondy[1] considers that this is due to adsorbed air preventing the water from wetting the capillaries readily but this can hardly be so because the capillaries have not dried out. It seems more probable that the water condenses first at the outside of the capillaries and that the hysteresis is due to the entrapped air or vapor. On this hypothesis the hysteresis should be less marked if the hydration and dehydration were carried on in the absence of air. This experiment has been tried[2] but without any striking results. The break at O was much less marked and the hysteresis loop was somewhat narrower; but it is not certain that this may not be due to differences in the preparation of the gel. Consequently there is no conclusive proof of the cause of the hysteresis. The matter is complicated further by the fact that O_2 does not always lie on the direct line from O_3 to O; but may sometimes be to the left of it. From the observed vapor pressures Anderson[3] calculates that the diameter of the pores is about 2.4–55$\mu\mu$. It has been suggested that OO_1 would be a flat if all the pores were of the same size. The water removed along O_1O_0 is probably the last film of water adsorbed on or in the capillaries. Zsigmondy considers that it may be water in solid solution in the silica; but this seems improbable because in that case this portion of the curve should be independent of the history of the sample which is not so, though there is nothing impossible about water forming a solid solution with quartz. Tammann[4] has shown that magnesium platinocyanide and zeolites do not lose their

[1] Kolloidchemie, 161 (1912). Spear's translation of this is inaccurate.

[2] Zsigmondy, Bachmann and Stevenson: Zeit. anorg. Chem., **75,** 189 (1912).

[3] Zeit. phys. Chem., **88,** 191 (1914).

[4] Wied. Ann., **63,** 16 (1897); Zeit. phys. Chem., **20,** 323 (1898).

water of crystallization at constant pressure and do not cloud. He assumes consequently that the water is present as a solid solution. This has been confirmed by Löwenstein[1] who found a similar behavior with strychnine sulphate and with the oxalates (but not the nitrates or sulphates) of cerium, lanthanum, erbium, yttrium, thorium, and zirconium. In these cases there is no evidence that the vapor pressures depend on the previous history of the sample.

If a silicic acid gel is heated, it sinters and contracts, thereby making the pores finer. They consequently do not hold so much water and owing to the change in structure they do not hold it so firmly. Consequently the whole diagram is moved to the left and the curve OO_1 becomes much shorter. If the silicic acid gel is allowed to stand for a long time at room temperature, there is a change in the walls of the capillaries such that the contraction of the gel on dehydration ceases at an earlier point. Under these circumstances the curve OO_1 becomes longer because the pores are coarser when they begin to empty. Since there is less water adsorbed strongly by the capillaries more water has to be removed before the pores are entirely empty.

That the curve OO_1 is not due to the presence of a definite hydrate is shown by the fact that the position and length of this curve are so variable and by the fact that similar optical phenomena can be observed when alcohol or benzene is substituted for water in the jelly. With alcohol two differences are noted in the pressure-concentration curve.[2] The break at O is not so marked and the point O_2 is far to the left of O, almost down to O_1. The significance of these two variations was not worked out by Anderson.

Holmes, Kaufmann and Nicholas[3] have shown that when a suitable silicic acid jelly is allowed to form in a glass test-tube, it vibrates like a rigid solid when tapped. Some of these gels gave a tone two octaves above middle C. The vibration frequency varies directly as the concentration of silicic acid, increases with excess of mineral acids, and decreases with excess of organic acid.

[1] Zeit. anorg. Chem., **68,** 69 (1909).
[2] Anderson: Zeit. phys. Chem., **88,** 191 (1914).
[3] Jour. Am. Chem., **41,** 1329 (1919).

The pitch does not vary with the length of the column of gel after a minimum length is exceeded. With gel columns 60, 90, and 120 mm in length and all 17 mm in diameter, the frequency was 1024 per second in each case, indicating that the vibrations are not longitudinal. With columns of the same length but of different diameters, the frequencies were 341, 640, 1024, and 1152 per second when the diameters were 34, 23, 17, and 15 mm respectively. The vibration frequency varies approximately inversely as the diameter and consequently the vibrations are transverse. When the gels were formed in vaselined tubes, they did not adhere to the walls and the vibration frequency was lower than for similar gels adhering to the glass walls. This shows that under ordinary circumstances the silica jellies are in a state of tension when formed in glass vessels and that this tension has an effect on the pitch of the tone which they emit when tapped.

It has been shown that a silica gel containing a great deal of water shrinks very much when the water is removed down to a certain point; but the volume change is not reversible. With a gelatine jelly the change is more nearly reversible. If dried gelatine is placed in cold water it swells a good deal and may take up ten times its weight of water; but there are no experiments to show that it would ever go up, say to an eight percent jelly. On the other hand it is possible to start with an eight percent jelly and dry it to a ninety-six percent jelly, after which it will take up water rapidly to an eight percent jelly. This means that the structure of the gelatine plays an important part in the rate of swelling. This is confirmed by some unpublished preliminary results by Mr. Cartledge. Gelatine jellies were made up containing 8, 16, 24 and 32 percent of gelatine. These were all dried at room temperature to about 96 percent concentration. When water was added, each swelled rapidly to the original concentration and then took up water slowly. If these results are accurate, it means that the four 96 percent jellies were all different and that the 8 percent gelatine did not become like the 16 percent, 24 percent or 32 percent gelatines while being dried. This is very important if true, because this possibility is usually overlooked. Arisz[1] finds that at 20° a half

[1] Kolloidchemische Beihefte, **7**, 1 (1915).

percent gelatine jelly disintegrates completely in water, a ten percent jelly goes to a two percent jelly in four days, a twenty percent jelly to a six percent one, a fifty percent jelly to a sixteen percent one, and an eighty percent jelly to a twenty percent one. Although the twenty percent jelly will take up enough water so that its composition is equal to that of a ten percent jelly, the two do not then behave alike. The jelly which has swelled until its composition is ten percent will not then take up as much water in a reasonable time as a jelly which is made up at ten percent. This shows that there is probably a difference in structure and in the way in which the water is held, although Sheppard considers that these phenomena are due to changes in the shape of the mass and to a consequent unequal distribution of water. Until we have some satisfactory theory to account for this difference in behavior, all experiments on the swelling of gelatine jellies in solutions of salts, acids and bases are likely to be misleading because one does not know to what extent the electrolytes are causing a change in structure. That a change in structure takes place even with water is shown by the experiments of Arisz on intermittent soaking. If two identical gelatine jellies are placed in water and one is kept in the water six days, while the other is in the water only on the first, fifth, and sixth days, the amount of swelling will be the same in the two cases within the limits of experimental error. While the partially swollen jelly is out of the water, some change in structure takes place such that it takes up water so much more rapidly than the other that the total swelling is the same in the two cases, although one jelly was soaked twice as long as the other. This seems to be a case without a moral because the hare caught up with the tortoise. Mr. C. R. Smith tells me that ash-free gelatine does not set to a jelly in cold water but comes out as a precipitate. This fact must be kept in mind in any discussion of the theory of the swelling of gelatine.

In certain salt solutions gelatine swells more than in water. With sodium salts the swelling decreases in the order $CNS > I > Br > NO_3 > ClO_3 > Cl >$ acetate $>$ citrate $>$ tartrate $> SO_4$. The last four cause a lesser swelling than in pure water. At a concentration of 13.8 percent NaCl the amount of water taken up passes through a maximum. Calcium chloride causes more swell-

ing than sodium chloride.[1] Gelatine swells more in dilute acid and dilute alkali solutions than in water or in salt solutions, the order for the acids being $HCl > HNO_3 > CH_3CO_2H > H_2SO_4 > H_3BO_3$. With the strong acids the swelling passes through a maximum for a given concentration and then decreases. Salts cut down the swelling both in hydrochloric acid and in caustic soda solutions, the order being the same in both cases. The chlorides, bromides, and nitrates have less effect in cutting down the swelling than do the sulphates and acetates. There is said to be no reversal of anions when one changes from an acid to an alkaline solution.[2] Fibrine behaves very much like gelatine though the amount of swelling is different and the order of the anions is not absolutely identical. Although a great deal of work has been done on the swelling of gelatine and fibrine[3] and some work on the adsorption by fibrine[4] and by gelatine,[5] very little has been accomplished along the line of developing a satisfactory theory. If we postulate that an adsorbed anion is the important factor, as seems to be the case with the salts, then the amounts of any two anions adsorbed must reverse as one changes from an acid to an alkaline solution. If an important factor is the adsorption of an undissociated salt, sodium and potassium salts should behave quite differently. It is probable that part of the difficulty is in the way that the experiments have been carried out. With fibrine, for instance, there is a maximum swelling at less than N/10 for hydrochloric acid, nitric acid, and sulphuric acid, whereas with acetic acid there is no sign of a maximum even with normal acid. If we compare dilute acids, say 0.02N, nitric acid and hydrochloric acid cause more swelling than acetic acid; but with normal acid the swelling is much greater in the case of acetic acid.[6] When sodium chloride is added to 0.015N solutions of

[1] This must refer to a slightly acid gelatine. In none of the work has the hydrogen ion concentration been controlled sufficiently carefully. Loeb has shown the importance of this; but his work, so far, has been with such dilute salt solutions that he did not detect any adsorption of the salt cation in acid solutions or of the salt anion in alkaline solutions.

[2] Fischer: Das Oedem, 37 (1910).

[3] Fischer: Jour. Am. Chem. Soc., **40**, 272, 292, 303 (1918).

[4] Tolman and Stearn: Ibid., **40**, 264 (1918).

[5] Dumanski: Zeit. phys. Chem., **60**, 553 (1907).

[6] Tolman and Stearn: Jour. Am. Chem. Soc., **40**, 264 (1918).

hydrochloric acid and acetic acid respectively until the salt concentration is normal, the swelling is about the same in the two cases; but the decrease in swelling is very much greater with the hydrochloric acid than with the acetic acid. Until some of these factors have been taken into account more thoroughly than has yet been done, it will be impossible to discuss the swelling of gelatine with any hope of success. It must be remembered that gelatine may cause hydrolysis of a salt with simultaneous but separate adsorption of base and acid. This certainly takes place with chromic sulphate solutions and may occur in other cases.

One must also keep in mind the possibility of metathetical reactions. Bechhold[1] cites an experiment in which 0.78 grams gelatine swelled in 100 cc of 0.05 HCl until it weighed 14.61 grams. The weight was only about 7 grams when the solution was also half-molecular with respect to potassium chloride and 2.84 grams when half-molecular with respect to potassium citrate. On the face of it, the potassium citrate has cut down the swelling a great deal more than the potassium chloride; but it is hardly fair to attribute this to the citrate ion exclusively, because the solution really had a much lower content of hydrogen ion than before and much of the decrease in swelling may have been due to that fact. The experiments of Fischer and Hooker[2] do not bear on this, because they kept the concentration of phosphate constant and varied the acidity and alkalinity. They found the greatest swelling at the acid and alkali ends with consequently a minimum at some intermediate point.

Jacques Loeb[3] considers that gelatine forms salts such as gelatine chloride or hydrochloride and sodium gelatinate, which he assumes forms true solutions. There seems to be no possibility at present of getting people to agree on a definition of true solution. It is therefore going to be necessary for somebody with an adequate knowledge of colloid chemistry to study the behavior of gelatine in detail and to see whether a better explanation can be given from that point of view. One set of experiments that Loeb made on the swelling of gelatine is very interesting.[4]

[1] Colloids in Pathology and Medicine, 69 (1919).
[2] Jour. Am. Chem. Soc., **40**, 272 (1918).
[3] Jour. Gen. Physiology, **1**, 39 (1918).
[4] Loeb: Jour. Biol. Chem., **31**, 343 (1917).

Cooper's commercial gelatine, when powdered, swells to a certain extent in water and to a slightly greater amount in M/8 sodium chloride. If the gelatine powder is treated for a short time with the salt solution and then with water it swells more than twice as much as in the salt solution or in water alone. Similar results were obtained with purified pig's bladder. Loeb considers that the first effect of the salt solution is to cause a chemical reaction between the colloid and the salt which would give rise to a great swelling if it were not checked by the salt solution. Replacing the salt solution by water makes possible the swelling due to the unspecified reaction between colloid and salt. This in itself does not mean anything. If only the colloid is changed, there is no chemical reaction between the colloid and the salt. If there is a chemical reaction, then all the salt will not be washed out and one would like to know what and how much was left in the gelatine. It seems probable that there was some hydrolysis, and that washing out the sodium chloride left the gelatine slightly more alkaline than before, in which case an increased swelling is what ought to take place. This hypothesis receives some confirmation from the fact that a preliminary treatment of pig's bladder with M/16 disodium tartrate caused nearly twice as much swelling as the preliminary treatment with M/8 sodium chloride. Since tartrate ions are presumably adsorbed much less by gelatine than chlorine ions, one would expect the gelatine to retain more alkali when treated with sodium tartrate than when treated with sodium chloride. The in reased swelling is therefore what might be expected. Before one can accept this explanation it is necessary to show experimentally that alkali is adsorbed in both cases and that more alkali is taken up from the tartrate solution than from the chloride solution. It has also been suggested that the preliminary treatment with the salt solution washed out some of the lime salts in the gelatine.

Loeb[1] has done a number of brilliant experiments which bring out clearly the importance of considering the hydrogen ion concentration in all work with gelatine. He finds that the isoelectric point for gelatine lies at a hydrogen ion concentration of 2×10^{-7}, or $pH = 4.7$ in Sörensen's logarithmic notation. Under the conditions of the experiments Loeb found that on the

[1] Jour. Gen. Physiol. **1**, 39, 237, 353, 483, 559 (1918–19).

acid side of the isoelectric point only anions of neutral salts are taken up and on the alkaline side of the isoelectric point only cations. Since the Hofmeister series calls for an effect due to both ions of a neutral salt on the swelling of gelatine, Loeb concludes that the Hofmeister series is a delusion and a snare. This does not follow at all. Loeb is working at such extreme dilutions that the specific effects of all ions but hydrogen and hydroxyl ions are practically negligible. In acid solutions only anions are taken up and in alkaline solutions only cations. Loeb recognizes the specific effect of iodine ions over chlorine ions in causing the liquefaction of gelatine; but he considers that liquefaction stands in no necessary relation to swelling, an assumption which will be shared by few. With higher salt concentrations Loeb will undoubtedly get entirely different results. His conclusions as to the existence of definite compounds depend on the assumption that he is dealing with true solutions and will fall with that assumption. While it is not possible to accept his theoretical conclusions, his experiments with silver nitrate and with potassium ferrocyanide, to take two striking cases, are marvellous as an example of technique. The so-called osmotic pressure measurements are apparently measurements of swelling and not of osmotic pressure.

Since the swelling and shrinking are practically reversible, the gelatine jellies do not become opaque at some point as was the case with the silica gels. Katz[1] has made some experiments on the vapor pressures of gelatine solutions. He obtained a smooth pressure-concentration curve with a point of inflection. With an 83 percent jelly the partial pressure of the water vapor was about half that of saturated water vapor and for a 90 percent jelly the partial pressure was about one-tenth that of saturated water vapor. The behavior of a gelatine jelly in liquid water and in saturated vapor has already been discussed elsewhere.[2] If the gelatine jelly is hardened somewhat by replacing the water with benzene,[3] it behaves in many respects like the silicic acid jellies.

The pressures that can be exerted by a swelling colloid may be very large. We know how a growing vine will displace stones. In

[1] Zeit. Elektrochemie, **18,** 800 (1911).

[2] See page 75.

[3] Bachmann: Zeit. Kolloidchemie, **23,** 85 (1918).

some experiments on dried seaweeds, it was found that water was taken up against a pressure of forty atmospheres and Rodewald states that starch will swell against a pressure of 2500 atmospheres. When gelatine dries in contact with glass, it may pull pieces of glass off the surface. Posnjak[1] has made some experiments on the amount of water with which gelatine is in equilibrium under different external pressures and on the corresponding behavior of raw Para rubber in different organic liquids. The data are given in Tables XLVIII–XLIX, the pressures being centimeters of mercury and the concentrations being grams of

TABLE XLVIII.—SWELLING OF GELATINE IN WATER

P = external pressure in cm Hg.
C = grams water per gram gelatine.

P	38.3	82.4	156	240	303	377
C	2.56	2.06	1.46	1.28	1.10	0.92

TABLE XLIX.—SWELLING OF RUBBER IN ORGANIC LIQUIDS

P = external pressure in cm. Hg.
C = grams liquid per gram rubber.

Liquid	P = 82.4 C	P = 156 C	P = 240 C	P = 377 C
Ether	2.40	1.79	1.49	
Benzene	4.41	3.28	2.72	2.09
Thiophene	5.32	4.00	3.32	2.71
Acetylene dichloride	7.35	5.22		3.42
Chloroform	9.31	7.07		4.58
Carbon tetrachloride	11.06	8.47	6.69	

liquid per gram of gelatine or rubber. As was to be expected, the liquid content decreases with increasing pressure. It would not be safe to extrapolate from these data to the pressures necessary to squeeze out the last drops of liquid; but they would evidently be very high. The specific effects of the different liquids are quite marked in the case of rubber, nearly five times as much carbon tetrachloride being taken up as ether. Owing to the differences in the densities of the two liquids, this is of course

[1] Kolloidchemische Beihefte, **3**, 417 (1912).

not a measure of the amount of swelling. With an external pressure of 156 cm Hg, Posnjak found that the amount of rubber in grams per liter was 283 with ether and 150 with carbon tetrachloride.

The taking up of liquid may be accompanied by a marked evolution of heat. In Table L are some figures by Rodewald for the heat evolved when starch swells in water.

Table L.—Heat Evolution with Starch and Water

$\%H_2O$	Calories per gram starch
0.23	28.11
3.23	20.97
8.16	12.43
12.97	7.37
19.52	2.91

We do not know at all what the solubility is of gelatine in water or of water in gelatine, except that it must be small. Experiments have been made to determine these values by pressing the gelatine and analyzing the supernatant liquid when a jelly contracts; but these data mean nothing because there is no proof that the so-called solution does not contain the substance in a colloidal form.

Diffusion

In dilute gelatine solutions the rate of diffusion of electrolytes is very nearly the same as in pure water; but this does not hold as the jelly is made more concentrated. The electrical conductance is also less in gelatine solutions than in water.[1]

Although diffusion takes place readily in gelatine jellies, some curious phenomena have been observed under special conditions. Liesegang[2] coated a glass plate with gelatine containing a small amount of potassium or ammonium bichromate. When a drop of concentrated silver nitrate solution is placed on the gelatine, the silver nitrate diffuses into the gelatine and reacts with the bichromate.[3] Instead of forming a continuous precipitate, the silver chromate comes down in concentric rings which are called

[1] Dumanski: Zeit. phys. Chem., **60**, 553 (1907).

[2] Chemische Reaktionen in Gallerten, **1898**.

[3] Bechhold: Colloids in Biology and Medicine, 261 (1919).

Liesegang's rings, or rhythmic banding. A similar experiment can be carried out in a test-tube and it is then possible to get as many as twenty or more parallel membranes. Ostwald[1] attempted to account for the phenomenon by supposing that the silver chromate remained in supersaturated solution, diffusing along with the silver nitrate until the metastabile limit is reached, when it precipitates. This ingenious hypothesis has not proved satisfactory, and there is as yet no entirely satisfactory explanation of the phenomenon. Microscopic examination shows that the apparently clear spaces between the concentric rings are not absolutely free from crystals of the insoluble compound, but contain very fine crystals. The phenomenon varies with the salt used, sodium chloride not giving rings, and with the nature of the jelly. The reaction between silver nitrate and potassium bichromate gives rings or layers in gelatine but not in agar, while lead nitrate and potassium chromate give layers in agar and not in gelatine. Neither of these reactions gives rise to layers in silicic acid,[2] though other reactions do. Bradford[3] believes that one of the reacting solutes is adsorbed by the layer of precipitate, thus giving a zone practically free from it. There is of course no objection to the assumption; but, as Hatschek points out, this explanation and that of Ostwald leave the specific effect of the jelly entirely out of account.

Rhythmic banding is important, because it is probable that something of this sort is the cause of the banded structure observed in agates and elsewhere. It is worth noting that Bechhold claims that the phenomenon does not necessarily have anything to do with diffusion because similar structures can be produced in jellies by crystallization of sodium phosphate or by freezing water. Holmes[4] has made a large number of crystallizations in silicic acid jelly. He has also put forward a theory of rhythmic banding,[5] which unfortunately does not account for the fact, recorded in the same paper, that colloidal gold gives three colored bands, red, purple and blue, before repeating.

[1] Lehrbuch allgem. Chemie, 2d Ed., **2,** 778.
[2] Hatschek: Second Report on Colloid Chemistry, 21 (1919).
[3] Biochem. Jour., **10,** 169 (1916); **11,** 14 (1917).
[4] Jour. Phys. Chem., **21,** 709 (1917).
[5] Holmes: Jour. Am. Chem. Soc., **40,** 1187 (1918).

CHAPTER IX

EMULSIONS AND FOAMS

Emulsions

When considering the adsorption of solids by liquids, it was pointed out that certain solids will pass into the interface between two liquids and will be held there quite firmly. This will also happen if the solid is present in so finely divided a state that it forms a colloidal solution in one or both of the liquid phases, as was found experimentally by Winkelblech[1] who, however, was very much puzzled by the phenomenon. He shook a dilute solution of gelatine with benzene and found a film of gelatine at the dineric interface. The method was so sensitive that 0.06 mg gelatine could be detected when working with 10 cc lots. Winkelblech proposed to use this as a method of analysis; but this is not satisfactory because the sensitiveness varies with changes in the gelatine or in the acidity of the solution. The more readily the substance is peptized by one of the liquids, the less readily it will go into the interface. We have already seen that solid gelatine is not peptized readily by water. Similar results were obtained with albumin, water-soluble starch, soap, colophonium, the proteins in beer, and with tannic acid, though not with gallic acid. As precipitating liquids could be used petroleum, liquid paraffin, benzene, carbon tetrachloride, and chloroform, but not ether. Winkelblech did not find out why ether did not work; but it is interesting to note that Miller and McPherson[2] found that arsenic sulphide forms a colloidal solution both in ether and in water, and that on shaking a colloidal solution of arsenic sulphide in water with ether, the colloid distributes itself through the two phases. Winkelblech also succeeded in the partial extraction of colloids from organic liquids by shaking colloidal solutions of fats with water, the fats forming a film at the interface.

[1] Zeit. angew. Chem., **18,** 1953 (1906).
[2] Jour. Phys. Chem., **12,** 706 (1908).

Biltz and Kröhnke[1] made some experiments to see whether the colloidal organic matter in sewage could not be extracted by shaking with organic liquids but they found that only about 30 percent went into the interface, so the method never came into technical use.[2]

In these experiments of Winkelblech the amount of organic liquid is large and the drops formed on shaking are not very small. The tendency is to form a coarse emulsion but this is not stable and cracks, the colloid then passing into the interface. An emulsion consists of drops of one liquid suspended in another liquid. When these drops are stabilized by an electrical charge they behave like any other colloidal solution of the same type.[3] In most cases there is an actual film around the globules and this keeps them from coalescing. It is evident that with any pair of non-miscible liquids there may be two sets of emulsions, one with drops of oil suspended in water and one with drops of water suspended in oil, the word oil being used here to mean the other liquid. The water-in-oil emulsion may be important in certain cases. Wa. Ostwald[4] has pointed out that if one treats wood with creosote emulsified in water, the water comes in direct contact with the wood, which is not what one wants. If one takes an emulsion of water in creosote, the creosote comes in direct contact with the fibers of the wood, which is much more satisfactory. It seems probable that in the case of a kerosene spray, one type is better than the other, though that point seems not to have been considered. The necessary conditions for forming a stable emulsion are that the drops shall be so small that they will stay suspended and that there shall be a sufficiently viscous film round each drop to keep the drops from coalescing. An emulsifying agent is therefore a substance which goes into the interface and produces a film having satisfactory physical properties. If the adsorption of the emulsifying agent lowers the surface tension on the water side of the interface more than it does on the oil side, the interface will tend to curve so as to be convex on the

[1] Zeit. angew. Chem., **20,** 883 (1907).

[2] Cf. Briggs: Jour. Phys. Chem., **19,** 210 (1915).

[3] Ellis: Zeit. phys. Chem., **80,** 597 (1912); Powis: Ibid., **89,** 91, 179 (1914).

[4] Zeit. Kolloidchemie, **6,** 103 (1910).

water side, and we shall have a tendency to emulsify oil in water. If the adsorption of the emulsifying agent lowers the surface tension on the oil side of the interface more than it does on the water side, the interface will tend to curve so as to be concave on the water side, and we shall have a tendency to emulsify water in oil. The simplest way then to emulsify oil in water is to add a water-soluble colloid which is adsorbed strongly at the interface and the simplest way to emulsify water in oil is to add an oil-soluble colloid which is adsorbed strongly in the interface. As a matter of fact this is the way in which almost all emulsions are made. Since most emulsifying agents will not peptize the liquid by themselves, it is usually necessary to break up the liquid into fine drops by some form of mechanical agitation.

Sodium and potassium oleates are water-soluble colloids and they are excellent for emulsifying oils in water. The gums are also water-soluble colloids and certain of them are much used in pharmaceutical work for emulsifying oils in water. Though gelatine is a water-soluble colloid, it is not used ordinarily as an emulsifying agent probably because there is too much danger of putrefaction. By adding salt to a soap solution, the soap film can be made to come out so brittle that it will not form a satisfactory emulsion.

Pickering[1] made emulsions of kerosene in water with small amounts of soap as the emulsifying agent. With 70–80 percent of kerosene, the mass was viscous and with 99 percent oil it was as stiff as blanc-mange, and could be cut into cubes which would stand alone. When a lump of this solidified kerosene was left standing in dry air, it liquefied because the water evaporated from the soap film which then cracked, letting the kerosene run out. The solidified alcohol which is so much used nowadays is not an emulsion, though it does contain some water. It is essentially an alcoholic soap jelly and presumably does not contain alcohol dispersed as drops.

Calcium and magnesium oleates form colloidal solutions in oil and can therefore be used to emulsify water in oil. Rosin and the resinates act in the same way and the water in ready-mixed paints is an emulsion of water as drops in linseed oil containing rosin. It is a simple matter to add fifty percent of water to a

[1] Jour. Chem. Soc., **91**, 2002 (1902).

ready-mixed white lead without changing the look of the mixture much, because the oil is the external phase. If water is stirred into a heavy lubricating oil containing a lime soap, the water will be emulsified in the oil and will change it to a grease, instead of decreasing the viscosity as might perhaps have been expected. Lanolin, or purified wool fat, will emulsify water and can easily be made to take up eighty percent of it. Nobody has determined what the emulsifying agent is in this case. Friedrich[1] proposes making printing inks with about half the normal content of linseed oil, turpentine, drying oils, etc. by diluting with water emulsified in wool fat and adding a little more coloring matter. The degras which is used in dubbing leather is apparently an emulsion of water in oil because Fahrion[2] states that normal degras should contain 15–20 percent water but that English sod-oil may run 30–40 percent water and the white degras from the German chamois leather works may go as high as 40–50 percent water.

The water in butter may be emulsified by means of a calcium soap; but more probably the water is merely dispersed as drops in a viscous medium without any true emulsion being formed. Milk is an emulsion with butter fat as drops in a water phase. It is possible to make imitation fresh milk by emulsifying renovated butter fat in skimmed milk. It is claimed that some day the milk problem of the large cities will be solved by shipping butter and a suitable milk powder to the cities and adding the water there, since there is a very large difference in cost between sending milk powder by slow freight and water by what is practically express, to say nothing of the difference in keeping qualities. Mayonnaise is an emulsion of oil in water with egg as the emulsifying agent. Cod-liver oil is of course an emulsion of oil in water.

It is not always easy to tell by inspection, whether water is external or internal phase in a given emulsion. A good way, devised by Briggs, is to examine the emulsion under the microscope,[3] stirring in gently a little water or a little oil. The one that is external phase will mix readily with the emulsion, while the other will not.

[1] Jour. Soc. Chem. Ind., **36,** 296 (1917).
[2] Ibid., **30,** 501 (1911).
[3] Newman: Jour. Phys. Chem., **18,** 34 (1914).

The emulsion jellies are of course all of the honeycomb type and it is a pity that none of them have yet been examined in the ultramicroscope. If they had been shown to be quite different in appearance from the gelatine and the silica jellies, for instance, this would have been a strong argument in favor of the view that the latter jellies are of a different type. If no marked difference could be discovered, as would undoubtedly be the case,[1] it would have been recognized long ago that the evidence of the ultramicroscope is worthless in matters of this sort.

In making emulsions of oil in water by means of sodium oleate, it must be remembered that the soap does not go entirely into the interface. There is always a relation between the concentration of the soap in the interface and the amount still peptized in the water.[2] It is a case of the distribution of soap between the water and the interface. Anything that cuts down the peptizing action of the water on the soap will increase the amount going into the interface and anything increasing the peptizing action of the water will decrease the amount of soap in the interface. It is not a question of osmotic pressure or of solubility.

While most emulsions are made with gelatinous colloids as emulsifying agents, this is not necessary theoretically. Anything that will go into the interface and make it sufficiently viscous will give the same result. If we can put enough of a fine powder into the interface, we shall have a plastic mass there, which will stabilize the emulsion. This has been done by Pickering[3] who obtained emulsions of oil in water using powdered, basic copper or iron sulphate as the emulsifying agents. The emulsions were not very good ones but they were emulsions. Sheppard[4] has obtained similar results, emulsifying nitrobenzene in aqueous sulphuric acid by means of lead sulphate. When mayonnaise is made with the powdered yolk of a hard-boiled egg, the resulting emulsion comes under this head. Schlaepfer[5] and Moore[6] have emulsified water in kerosene by means of carbon black.

[1] Bachmann: Zeit. Kolloidchemie, **23,** 89 (1918).
[2] Briggs: Jour. Phys. Chem., **19,** 210 (1915).
[3] Jour. Chem. Soc., **91,** 2010 (1907); Zeit. Kolloidchemie, **7,** 14 (1910).
[4] Jour. Phys. Chem., **23,** 634 (1919).
[5] Jour. Chem. Soc., **113,** 522 (1918).
[6] Jour. Am. Chem. Soc., **41,** 940 (1919).

The pharmacists make great use of emulsions of oil in water and the books on pharmacy are filled with elaborate details as to the method of making emulsions. There are two general methods in vogue and both give good results, although they appear mutually contradictory. In the American method the gum, which is used as an emulsifying agent, is peptized and the resulting colloidal solution is placed in a large mortar. The oil is added a little at a time or in four separate portions with continuous stirring. If one starts stirring to the right, one must continue stirring to the right or no emulsion will be formed. Some books go so far as to say that a left-handed man cannot make an emulsion, but that seems a bit absurd. In the Continental method, the gum is ground in a mortar with the oil, in which it does not dissolve, and enough water to emulsify all the gum is then added at once.

Since the essential condition for making an emulsion is to break the oil into sufficiently fine drops and coat them with the gum solution, there is no necessary reason for adding the oil in separate portions in the American method. When the constituents are mixed in a bottle and shaken in a shaking machine, it is easy to make an emulsion if the amount of oil is not too large. With a mechanical shaker[1] giving 400 shakes per minute and a one percent solution of sodium oleate, 80 percent by volume of benzene could be emulsified in fifteen minutes but it took two hours to emulsify 96 percent of benzene, and 99 percent of benzene was not completely emulsified after eight hours of continuous shaking. If the shaking is done intermittently by hand so that the unemulsified benzene can separate at intervals, the number of shakes can be cut down enormously, from 48,000 to 80 in the case of the 96 percent emulsion and from 6000 to 7 in the case of the 80 percent one. Continuous shaking in a bottle disintegrates both benzene and soap solution into drops, the latter of which is disadvantageous. Since the soap solution is the continuous phase in these emulsions, any treatment which breaks up the soap solution retards emulsification. When benzene is dispersed into drops in the soap solution, the soap coats the drops and prevents them from coalescing, while there is nothing to prevent the rapid coalescing of the water drops in the benzene. The first few shakes cause the most disintegration of

[1] Briggs: Jour. Phys. Chem., **24**, 120 (1920).

the benzene and the least disintegration of the soap solution; consequently intermittent shaking gives the best results. The pharmacist was doing intermittent stirring unconsciously when he added the oil in separate portions. The reason for using a mortar that is apparently much too large is to get a large surface and thus to facilitate emulsification. A similar result can be obtained by putting the mixture in a cylindrical glass bottle, with or without glass beads, and rolling the bottle.

These experiments throw some light on the making of mayonnaise. Since mayonnaise is essentially an emulsion of oil in water (vinegar) with egg as the emulsifying agent, it ought to behave like any other emulsion and so it does for the experts in the Departments of Home Economics. They can add the ingredients in any order, all at once or in separate portions, hot or cold, and the mayonnaise always comes. On the other hand, these same experts do not train their pupils so that these latter can make mayonnaise every time. It seems certain that the experts do something or other unconsciously which they consequently do not tell to their pupils. Probably the expert is so sure of the result that she works leisurely without being hurried or flurried, and is practically doing intermittent stirring. The person who is not an expert and who is uncertain of the outcome probably goes at her task so vigorously as to defeat her object in many cases. While this explanation has not been tested, one expert said that she had found that if the materials were beaten well together and then allowed to stand for a moment or two, a couple of swishes would make the mayonnaise. I have been told that Béarnaise sauce is an emulsion of melted butter in tarragon vinegar without any egg and that it is very easy to make. If this is so, tarragon vinegar must contain a good deal more of some emulsifying material, probably a tannin, than ordinary vinegar.

The Continental method of making emulsions has also been studied by Briggs[1] who finds that the object of grinding the oil with the solid gum is merely to increase the interface between oil and water by suspending in the oil finely divided solids which are wetted preferentially by water. The gum acts both as finely divided solid and as emulsifying agent. It is possible to

[1] Jour. Phys. Chem., **24**, 147 (1920).

get the same results by grinding the oil with sand and adding a colloidal solution of gum, but the resulting emulsion then contains the sand.

Since sodium oleate emulsifies oil in water and calcium oleate emulsifies water in oil, a mixture of the two oleates will behave differently, depending on the relative amounts. There will also be some ratio of calcium to sodium at which the two oleates will practically balance each other and the slightest relative change will change the type of the emulsion. This has been proved experimentally by Clowes[1] who worked with a sodium soap and calcium chloride. This antagonistic action of sodium and calcium salts with reference to emulsions throws light on some perplexing physiological problems. Jacques Loeb showed that certain marine organisms died in sodium chloride or calcium chloride solutions which were isotonic with sea-water; but flourished when there was a definite ratio of sodium to calcium, a result which could not be explained on the basis of osmotic pressure. If we consider protoplasm as consisting of lipoids (oil) and water, we shall have an emulsion of oil in water in presence of sodium salts and of water in oil in presence of calcium salts. When the sodium and calcium salts are present in a definite ratio, there will be a balancing between these two types of emulsion, and it may well be that this critical state is the one which is conducive to life and growth. As a matter of fact, Clowes found that the ratio of sodium and calcium salts necessary to produce a balancing between the two types of emulsions when working with oil, water and soap, was practically the same as that found in sea-water. This indicates a very close connection between the two sets of phenomena. Osterhout[2] at Harvard has shown that the specific electric conductivity of certain seaweeds is increased by addition of sodium salts and decreased by the addition of calcium salts. If the hypothetical emulsion changed to one of oil in water, the conductivity should increase, and it should decrease if the emulsion changed to one of water in oil. Clowes[3] has succeeded in duplicating Osterhout's results by impregnating filter paper with an emulsion

[1] Jour. Phys. Chem., **29,** 407 (1916).
[2] Science, (2) **35,** 112; **36,** 350 (1912).
[3] Proc. Soc. Exp. Biol. Med. **15,** 108 (1918).

of oil, water, and soap, to which he afterwards added sodium and calcium salts.

When a badly made emulsion is allowed to stand, it decomposes progressively. This seems to be due to the fact that when the free oil comes in contact with the film around the oil drops, it tends to make it bend in the opposite direction, thereby cracking the emulsion. Temperature changes probably play a part in causing the ageing and cracking of the films; but there has been no careful study of this point. All we know is that anything which destroys the film destroys the emulsion. That is why acid destroys a soap emulsion. In the case of oil emulsions in water, we get cataphoresis and the emulsions can be broken down by the action of a high-tension direct current.[1] In the oil industry emulsions of one kind and another are a common occurrence and their removal is quite an important matter. Very little that is accurate has been published in regard to this.

One interesting case in the technical application of emulsions is the splitting of fats by superheated steam in the presence of lime. Caustic soda is not effective because it is necessary to use so much; but one percent of lime is sufficient to cause complete hydrolysis. No explanation of this has been tested out; but it seems certain that the calcium soap emulsifies the water in the fat. This may give a sufficiently intimate mixture to hydrolyze the fats or the water globules may pass into steam, breaking down the emulsion which then forms again. Whatever the secondary details may be, it is clear that the formation of an emulsion of water in oil is the essential thing because the oxides of magnesium and of zinc act in a similar way.

Foams

In an emulsion of oil in water we have drops of oil coated by a more or less viscous film containing water, with water outside. If the emulsion is not sufficiently fine, the emulsified oil will rise to the surface and we get a sort of cream, which consists almost entirely of the oil drops with their viscous coating and with little or no free water. If we consider the globules of oil replaced by air, we shall have a mass of froth, the only difference that the

[1] Fanto and Stritar: Jour. prakt. Chem. (2) **81**, 564 (1910).

bubbles would be much finer than in the ordinary froth. The conditions for forming froth should then be much the same as for forming an emulsion and that is the case, though there are of course some differences.

It has already been shown that colloidal solutions of peptone form a film of solid peptone over the surface[1] and that the surface viscosity of a saponin solution is 60 times that of the mass of the liquid. The formation of a film at the surface depends primarily on the adsorption of the colloid at the interface and not on the presence of air. On the other hand the adsorption of air by the colloid will cause the latter to rise more rapidly and will also help to keep it there. This effect might be so strong as to give rise to a film at the surface in certain cases where none would be formed otherwise. Stark[2] has called especial attention to the adsorption of air by colloidal particles. We know that gum arabic adsorbs air strongly and sodium palmitate likewise. Findlay[3] has shown that carbon dioxide is taken up under some conditions by starch solutions.

Freundlich[4] considers that no pure liquid can foam and in this he is apparently right. He then deduces that a low vapor pressure, a low surface tension, and a high surface viscosity are essential to foam. The low vapor pressure is put in avowedly because a foam with a volatile liquid like ether would evaporate very rapidly. That is not necessary because we can work in closed vessels. Freundlich has put in the low surface tension because all the foaming solutions which he knew about had lower surface tensions than the pure liquid; but this criterion is not sound because salt solutions will foam. Since salts may increase the fluidity of water, a high surface viscosity is not essential. All three of Freundlich's criteria thus go by the board, which shows the danger of the empirical generalization. On the other hand Freundlich's criteria do hold in practically all cases if one confines oneself to fairly permanent foams, which was what he was really considering.

To get a foam the only essential is that there shall be a distinct

[1] See page 189.

[2] Wied. Ann., **68,** 117, 618 (1899).

[3] Jour. Chem. Soc., **101,** 1459 (1912); **103,** 636, 1170 (1913).

[4] Kapillarchemie, 302 (1909).

surface film, in other words, that the concentration in the surface layer shall differ perceptibly from that in the mass of the liquid. All true solutions will therefore foam if there is a marked change of surface tension with concentration, regardless whethert he surface tension increases or decreases. All colloidal solutions will foam if the colloid concentrates in the interface or if it is driven away from the interface. To get a fairly permanent foam the surface film must either be sufficiently viscous in itself or must be stabilized in some way. This can be done by introducing a solid powder into the interface.

Solutions of aqueous alcohol, acetic acid, sodium chloride, and sulphuric acid all foam when shaken; but the foam is instable. Soap solutions foam when shaken and the foam is, or may be, quite stable owing to the viscosity of the soap film. With saponin the surface film is even more stable. If we add to aqueous alcohol some substance like lycopodium powder which goes into the interface, we get a stabilized foam. We can do the same thing with aqueous acetic acid by adding lamp-black. The presence of enough of a finely divided solid in the interface will make the film so viscous that the foam will be quite stable. Grease will help stabilize a foam in some cases and it has been claimed erroneously that the foaming of sulphuric acid solutions is due to grease.[1]

In 1857 Gladstone[2] pointed out that aqueous solutions of organic substances are apt to froth and he cited beer as a then familiar instance. He did not realize however that it was the colloidal matter in the beer which caused the frothing. It has been shown by Zeidler and Nauck[3] that removing the albumoses from beer destroys the foaming. Gladstone showed, however, that the dissolved air was not essential to the frothing. If this were pumped out in a vacuum, the liquid frothed freely when shaken with air. Gladstone states that aqueous solutions of the acetates of iron, copper, lead, and other metals froth readily, especially the ferric acetate solution. As we know, this is the one which hydrolyzes most readily and the frothing is due undoubtedly to the combined effect of the acetic acid and the hydrous ferric oxide.

[1] Lang: Ber. deutsch. chem. Ges., **18,** 1391 (1885).
[2] Phil. Mag. (4) **14,** 314 (1857).
[3] Jour. Soc. Chem. Ind., **20,** 260 (1901).

Ramsden[1] obtained precipitation of solids by shaking solutions of albumin, proteins, gelatine, cupric acetate, ferric acetate, mastic, etc. This is essentially the same in principle as Winkelblech's later experiments with a second liquid phase. The colloid goes into the surface, forming a solid film which is so brittle, however, that it does not give a good emulsion or foam. When the emulsion or foam cracks, the colloid does not go back at once into colloidal solution; but remains as a precipitate. An interesting case of this is to be found in the behavior of enzymes. Many enzyme solutions can be rendered inactive merely by shaking.[2] A rennet solution need be shaken violently in a test tube for only two minutes to destroy most of its power to coagulate milk. The inactivation was found to be a surface phenomenon, the inactivation increasing with the length of time and the violence of the shaking. The volume of air, the concentration of the enzyme and the temperature are all influencing factors. The enzyme concentrates in the foam and on the walls of the vessel. Vanino and Hartl[3] shook up a red colloidal solution of gold and found that the gold first turned blue and then precipitated as brown gold. The irreversible formation of a film on agitation with air is an important thing in making whipped cream. It seems probable though not proved that we might get tiny air bubbles emulsified in a liquid, in which case the air in the bubbles would be given off relatively slowly when the pressure was relieved.

If we have two colloids present, one of which goes into the interface more readily than the other, the first may keep the second out more or less completely. Herty and Willard[4] found that resene cuts down soap lather while it has been shown that shaking does not inactivate a rennet solution to which saponin has been added because the latter keeps the rennet from going into the interface.

Under adsorption of solid by liquid, reference was made[5] to the Elmore bulk oil process of ore flotation where the sulphide

[1] Proc. Roy. Soc., **72,** 156 (1903); Zeit. phys. Chem., **47,** 336 (1904).
[2] Bechhold: Colloids in Biology and Medicine, 189 (1919).
[3] Ber. deutsch. chem. Ges., **37,** 3623 (1904).
[4] Jour. Ind. Eng. Chem., **6,** 895 (1914)
[5] See page 89.

ore went chiefly into the interface between oil and water while the siliceous gangue settled to the bottom. This was an expensive process technically because it called for about one ton of oil per ton of ore. The Minerals Separation Company holds a patent for ore separation using only a fraction of one percent of oil per ton of ore, a froth being formed which carries up the values. If no ore is present, bubbles of air are formed coated with a thin film of oil, around which is water. The oil film is not viscous enough to form a stable froth. If we introduce particles of sulphide ore into the oil-water interface or into the oil itself, we get a stabilization of the film because we then have practically an armor-plated bubble. The resulting froth can be scraped or shovelled off. It is said that about sixty million tons of ore are handled by this process every year in America alone. In most cases acidification of the solution and rise of temperature increases the effectiveness of the separation. A blended oil seems often to give better results than a straight oil. One oil may spread better over the surface and be a more effective frothing oil, while a second oil may have a greater effect in carrying the sulphide particles into the interface. Although a good deal of experimenting has been done with this process, the theoretical results are not what they should be, apparently because people have insisted upon looking upon the whole thing as very mysterious. This is one of the many industries involving colloid chemistry where the art is far ahead of the science. In Australia eucalyptus oil has proved very successful. In this country so-called pine oil has been used a great deal with or without admixture of mineral oils. While sulphide ores are the ones which have been worked with the most, the principle is a general one, and the Calumet and Hecla Mining Company are reported to be using the process for removing native copper from the tailings.

If the amount of air is insufficient, the oil may cause the ore particles to agglomerate and sink. This was patented by Cattermole but is not technically so successful as the frothing process. If the amount of air is excessive relatively to the ore, the number of bubbles will be so great that the ore particles cannot coat them sufficiently to armor-plate them; the bubbles will therefore be instable. This principle is involved in the Callow process. Air is introduced in fine bubbles at the bottom of the cell These

bubbles float up the ore particles but break as soon as they reach the surface. The ore particles must be removed before they settle back. We can therefore have clotted particles, armor-plated bubbles, or fragile bubbles, depending upon the conditions.

The flotation process will not work with large lumps because the force of gravity would carry them down. One of the advantages of the method is that it will work with finely ground material. On the other hand there is a limit. It is customary to say that the ore goes into the interface and the gangue does not; but that is not to be taken too literally. Some gangue always goes into the interface and the percentage increases the finer the gangue. The ideal condition therefore is one in which the gangue is coarse relatively to the ore particles.

That the essential thing is the adsorption of the particles at the oil-water interface is shown by the fact that the introduction of saponin kills the flotation of the ore under ordinary conditions although it increases the frothing tremendously.

A carbon dioxide froth, made from aluminum sulphate and sodium bicarbonate, is used for putting out fires. It is not successful against burning aluminum powder for two reasons. The aluminum powder is floated up by the froth and consequently not blanketed by it. Also hot aluminum powder reduces carbon dioxide to carbon monoxide which then burns in the air. Fortunately few fires are due to aluminum powder. The alumina froth is said to be stabilized by the addition of other colloids such as licorice; but no details have been published.

CHAPTER X

NON-AQUEOUS COLLOIDAL SOLUTIONS

Very little systematic work has been done on sols and gels with liquids other than water. Graham replaced the water in a silicic acid jelly by alcohol, sulphuric acid, nitric acid, and formic acid. Van Bemmelen substituted acetone for water, while Bachmann[1] put in benzene. Bütschli replaced the water in gelatine and agar jellies by alcohol, for which could then be substituted chloroform, turpentine or xylene.

We know that the calcium and magnesium oleates form colloidal solutions in organic liquids and that the so-called resinates do the same thing. It is very probable, though not proved, that stearin exists in colloidal solution in olive oil. The whole industry of the cellulose nitrates and cellulose acetates depends upon the formation of colloidal solutions in organic solvents. Pieroni and Girardi[2] have studied some colloidal solutions in pyridine. Water can be emulsified in lanolin and in linseed oil. Svedberg[3] has prepared colloidal solutions of metals in ether, pentane, isobutyl alcohol, etc. Schneider[4] has made alcoholic solutions of colloidal silver and finds that they are coagulated at once by isopropyl alcohol, normal and secondary butyl alcohol, trimethyl carbinol, and heptyl alcohol, but not by propyl or isobutyl alcohol. Colloidal sulphur may be formed when sulphur chloride reacts with ethylene.[5] Michael[6] obtained colloidal sodium chloride without knowing it by the interaction of chloracetic ester and sodium malonic ester, while Paal[7] showed

[1] Zeit. anorg. Chem., **03,** 165 (1911); Anderson: Zeit. phys. Chem., **77,** 191 (1914).

[2] Zeit. Kolloidchemie, **15,** 159 (1914).

[3] Ber. deutsch. chem. Ges., **38,** 3616 (1905); **39,** 1705 (1906).

[4] Ibid., **25,** 1281 (1892).

[5] Conant: Jour. Am. Chem. Soc., **42,** 585 (1920).

[6] Ber. deutsch. chem. Ges., **38,** 3217 (1905).

[7] Ibid., **39,** 1436, 2859 (1906); **41,** 51 (1908); **42,** 277 (1909).

that petroleum ether precipitated the sodium chloride, which would go again into apparent solution on treatment with benzene. Copper oleate[1] stabilizes a colloidal solution of cupric chloride in benzene.

It seems probable that trinitroxylene (TNX) is peptized by trinitrotoluene (TNT) for Marshall[2] says that when 30–50 parts of TNX were suspended in 70–50 parts of TNT, the mass was sufficiently fluid to be cast without the use of any extruding mechanism. The cooled castings appeared amorphous and resembled paraffin in texture. The castings showed no segregation of either constituent, were free from air-holes, were of uniform density, were non-hygroscopic, and showed no tendency to become oily or leaky on storage. They could be detonated completely with smaller primers of tetryl than could castings of TNT alone.

Bechhold[3] has been able to separate some of the asphalt out of a crude oil by ultrafiltration through a toluene-glacial acetic acid collodion filter. Amberger has made colloidal solutions of several metals in lanolin. Richardson[4] finds that asphalt from certain sources contains solid particles dispersed in the asphalt. Lorenz[5] has shown that the fused baths, from which we obtain sodium, aluminum, and other metals, electrolytically, tend to peptize the molten metal. The amount of peptization or production of metallic fog increases very rapidly with rising temperature, which is one reason why it is very important to carry on the electrolysis at as low a temperature as possible. In the glass industry colloidal solutions are very common, with stannic oxide, gold, copper, etc., as the dispersed phase.

During the war a colloidal fuel was developed, consisting of coal in fuel oil. Since the mixture is denser than water, a fire can be put out by spraying with water, so that the fire risk is claimed to be less than with oil fuel. Shoe blacking is another case of a colloidal solution with a non-aqueous solvent. Acheson oildag is a third variant of the same general type.

[1] Von Weimarn: Kolloidchemische Beihefte, **1**, 409 (1910).

[2] Jour. Ind. Eng. Chem. **12**, 248 (1920).

[3] Colloids in Biology and Medicine, 11 (1910).

[4] Jour. Phys. Chem., **19**, 241 (1915); Rosinger: Zeit. Kolloidchemie, **15**, 177 (1914).

[5] Van Bemmelen Gedenkboek, 395 (1910).

CHAPTER XI

FOG AND SMOKE

Fog

A fog consists of drops of liquid suspended in a gas, usually air, while a smoke has solid particles. To obtain a fog a vapor must be saturated suddenly, so that condensation takes place more or less uniformly throughout the mass. On a laboratory scale this cooling can best be brought about by an adiabatic expansion or by letting a jet of steam emerge into a cooler atmosphere. The first method is the more satisfactory for quantitative measurements and the second for qualitative determinations. If the supersaturation is excessive, the liquid comes down as a dense fog without presenting any specially interesting characteristics. If the supersaturation is slight, it is found that no fog forms unless "nuclei" are present in the air. This matter was studied with great thoroughness by Coulier[1] who showed that there is almost always dust in the air and that condensation takes place on the dust particles. The dust can be removed by filtering the air through cotton. Ozonized air is active in causing condensation and this activity is not destroyed by filtering the air through cotton. Oxygen, hydrogen, and nitrogen become active when heated and this activity is not destroyed by filtration. There are therefore other types of nuclei besides solid particles.

It was found by R. v. Helmholtz[2] that the vapors of sulphuric acid, hydrochloric acid, and sulphurous acid act as nuclei. In a later paper R. v. Helmholtz and Richarz[3] advance the view that condensation occurs frequently during chemical reactions even though the reacting substances and reaction products do not act as nuclei. They point out that neither ozone nor oxygen acts

[1] Jour. Chem. Soc., **29,** 186 (1876); Aitken: Trans. Roy. Soc. Edin., **30,** 337 (1883).

[2] Wied. Ann., **27,** 508 (1886).

[3] Ibid., **40,** 161 (1890).

as a nucleus but that nuclei are present while ozone is decomposing. A similar phenomenon was observed in the case of a number of slow oxidations and reductions. Hydrochloric acid and ammonia are said not to act singly nor does ammonium chloride; but ions are formed during the reaction. This statement in regard to hydrochloric acid contradicts the previous statement as to this substance but there is a difference of concentration and the authors are also willing to admit that some ammonia in the air may have reacted with the acid in the earlier experiments. On this statement of facts the authors conclude that the reactions pass through an intermediate stage in which ions are formed, and that these ions act as nuclei. This extremely interesting hypothesis is put on the defensive by the experiments of Engler and Wild[1] who claim that solid substances are the real nuclei in all these cases, iodine pentoxide in the oxidation of iodine, an oxide of phosphorus in the oxidation of phosphorus, ammonium chloride, etc. Helmholtz and Richarz made a good deal of the fact that the nuclei could not be suspended solids because they were not removed when the gases were bubbled through water. Engler and Wild point out that the solids in the centre of the gas bubbles do not come in contact with the water at all and that it is a simple matter to carry suspended particles of phosphorus pentoxide through several wash-bottles in spite of its tremendously hygroscopic nature. The difficulty of removing suspended solids is shown by the special precautions necessary to stop such toxic smokes as diphenylchlorarsine.

Pringal[2] considers that the nuclei attributed to ozone are really oxides of nitrogen and believes that ozone oxidizes nitrogen to some extent. Bieber[3] concedes that oxides of nitrogen will act as nuclei; but shows that they are not formed by the action of ozone on nitrogen, and that the oxides of nitrogen do not form the stable, blue cloud which is observed so often when working with ozone. He attributes this stable, blue cloud to hydrogen peroxide, showing that the cloud is formed when hydrogen peroxide is present and that it does not occur under conditions which preclude the formation of hydrogen peroxide. Thus we

[1] Ber. deutsch. chem. Ges., **29,** 1929 (1896).
[2] Drude's Ann., **26,** 727 (1908).
[3] Ibid., **39,** 1313 (1912).

do not get it with water vapor alone or with water vapor plus a gas other than oxygen. Now hydrogen peroxide can be formed by the action of ultra-violet light on water, especially on liquid water, according to the equation $H_4O_2 = H_2O_2 + H_2$. It may also be formed by the action of ultraviolet light on a mixture of hydrogen and oxygen,[1] according to the equation $H_2 + O_2 = H_2O_2$. This second reaction of course plays no part in the case under consideration. Bieber rules out the first one because no hydrogen is formed in presence of ozone, and consequently he believes that the reaction is $H_2O + O = H_2O_2$, where the oxygen atom is the third one in ozone or is set free from oxygen by ultra-violet light. While this may be true, it is not necessarily so. It is quite as simple to consider that the ozone acts as a depolarizer to the nascent hydrogen since it is very improbable that the action of ultraviolet light could give rise to the reaction $H_4O_2 + O_3 = H_2O_2 + H_2O + O_2$, because we know that the intermediate product, electrically neutral monatomic hydrogen, reacts with oxygen.

Haber and Just[2] have shown that when the alkali metals react with different gaseous substances such as water vapor, hydrochloric acid, iodine, phosgene, oxygen, thionyl chloride, etc., negatively charged particles are set free in the reaction zone and can be removed from it by an electric field. When the pressure of the reacting gas is very low, the negative particles pass out from the reaction zone of their own accord and prove to be chiefly free electrons. In presence of light there is an enormous increase in the emission of electrons. Similar results were obtained with silver, copper, and aluminum when heated or when the pressure or the gas was very low.

While these experiments of Haber and Just prove conclusively that electrons are emitted during some chemical reactions, they do not prove at all that there is always an intermediate formation of ions in every chemical reaction. On the other hand, we do know that gaseous ions, if present, may act as nuclei. As Donnan[3] points out, the very interesting experiments of C. T. R. Wilson[4]

[1] Fischer and Wolf: Ber. deutsch. chem. Ges., **44,** 2956 (1911).
[2] Zeit. Elektrochemie, **16,** 275 (1910); Just: Ibid., **20,** 483 (1914).
[3] Phil. Mag. (6), **8,** 306 (1902).
[4] Phil. Trans., **189A,** 265 (1897); **193A,** 289 (1899).

on the condensation of water vapor in the presence of dust-free air and other gases, have rendered it extremely probable that this condensation occurs around electrical nuclei of some sort. It was found that an adiabatic expansion produced no condensation in dust-free air saturated with aqueous vapor until the expansion reached the value of 1.25. This expansion (ratio) produced a small shower of fine rain, and expansions ranging from the above value up to 1.38 produced small fine showers of not much greater density. At an expansion of 1.38, however, the phenomenon changes in character, and a more or less dense fog is produced. Now air or any other gas exposed to Röntgen rays becomes a conductor; and the experiments of J. J. Thomson and his fellow-investigators have made it practically certain that this conduction is of a convective nature, due to electrically charged nuclei in the gas. The importance of this lies in the fact that Wilson's experiments showed that air which was saturated with water vapor and exposed to Röntgen radiations gives, when expanded adiabatically, no condensation before the expansion 1.25, and a dense fog instead of a fine rain at that point. The natural conclusion is that the rain-like condensation for expansions ranging from 1.25 to 1.38 is due to condensation on a comparatively small number of electrical nuclei either existing in the gas or produced by the sudden expansion. Donnan was especially interested in the fact that here is a "case of condensation of a vapor of a liquid of unique ionizing power round electrical nuclei. It becomes a matter of interest to compare with water vapor the vapors of other liquids whose ionizing powers are either much smaller or practically zero." He came to the conclusion that organic liquids condensed on ions less readily than does water.[1]

When a gas is previously saturated with water vapor, the lowering of the pressure necessary to produce condensation by adiabatic expansion[2] is about 15 cm for air, oxygen, and nitrogen, but about 21 cm for hydrogen. Condensation of water takes place more readily on negative ions than on positive ions;[3] the reverse is true for alcohol.[4] In dust-free and ion-free gases which do

[1] Cf. Barus: Phil. Mag. (6), **4**, 262 (1902).
[2] Bieber: Drude's Ann., **39**, 1313 (1912).
[3] Wilson: Phil. Trans., **193A**, 289 (1890).
[4] Przibram: Phys. Zeit. A., **8**, 561 (1907).

not react with water vapor, the condensation takes place much less readily, at an eight-fold supersaturation according to Wilson.

With water vapor the expansions 1.25, 1.28, 1.31, and 1.38 are the values: (*a*) to start catching the negative ions; (*b*) to catch all the negative ions; (*c*) to start catching the positive ions; (*d*) to catch the nuclei of cloudy condensation.[1]

Since gaseous ions act as nuclei[2] it is not surprising that condensation may take place when inert air is exposed to cathode rays, Röntgen rays, Becquerel rays or ultra-violet light; also when a spark discharge or a silent discharge passes through the air. The ions given off by heated metals may also act as nuclei.

Broadly speaking, the nuclei consist of very hygroscopic substances, solids, and ions.[3] The hygroscopic substances form solutions having a very low vapor pressure and the water vapor is excessively supersaturated when they are present, consequently condensation takes place. Freundlich[4] accounts for the behavior of suspended solids by postulating that they have concave surfaces on which water would have a lower vapor pressure than on a convex surface and consequently would precipitate more readily. This is very ingenious but carries with it the corollary that solid spheres would not act as nuclei. While this may be true, it is not probable. It seems much simpler to consider that water vapor is adsorbed by the suspended solid, forming the equivalent of a liquid surface on which the further excess of water vapor condenses. It has been shown by J. J. Thomson[5] that the effect of electrification of a drop of liquid is to decrease the vapor pressure of the liquid. Consequently water vapor will tend to precipitate on an ion as a nucleus, which is what happens experimentally.

While fog usually consists of condensed water, there are conditions under which special types occur. Thus Frankland[6] describes what he calls dry fog. Dense fogs have been noticed

[1] Quoted from Wilson by Owen and Roberts: Phil. Mag. (6), **23,** 352 (1912).

[2] Freundlich: Kapillarchemie, 294 (1909).

[3] For a recent general discussion, see Rothmund: Monatsheft für Chemie, **39,** 571 (1918).

[4] Kapillarchemie, 295 (1909).

[5] Application of Dynamics to Physics and Chemistry, 166 (1888).

[6] Proc. Roy. Soc., **28,** 238 (1879).

around London when the degree of saturation was only 50–80 percent. Frankland believed that this was due to films of oil from coal smoke coating the drops of water and retarding the evaporation. While Frankland's explanation of the dry fogs is probably the correct one, there are two possibilities which are not covered by the experiments. He has not shown that the oily or tarry matters condense on the drops of water. It is certain that, under some conditions, the water vapor might condense on the oily drops as nuclei, in which case the water would be outside and not inside. He has also not considered the possibility of the "dryness" being due to a lowering of the vapor pressure of the drops by the dissolving in them of sulphur dioxide, sulphuric acid, etc. While it is not probable that sufficiently concentrated solutions would be formed in this way to produce so great an apparent dryness, yet it is very probable that this is at least a contributing factor.

At times a special state of things occurs at the seashore. If the wind blows very hard from the sea, a heavy surf springs up and salt spray is carried inland. Ordinarily this does no harm to vegetation because a wind of this sort is usually accompanied by rain which dilutes the spray sufficiently to make it harmless. One summer at Newport, R. I., the wind blew hard from the south for sixty hours without any rain. The result was that undiluted salt spray was carried inland in enormous quantities. Everything was coated with salt; and trees, shrubs, and plants were burned brown for nearly half a mile from the shore. At Cirencester in England the wind causes an average annual deposit of thirty-six pounds of sodium chloride per acre.[1]

Supercooled fogs seem also to occur at times.[2] On Ben Nevis the top of the hill in ordinary weather is enveloped in drifting fog. When the temperature of the air and ground is below freezing, this fog deposits feathery crystals of ice on every surface that obstructs its passage. A round post will have an almost uniform crop of crystals on its windward half, pointing so accurately to windward that it is possible to trace changes in the direction of the wind from the successive layers of crystals lying at different

[1] Von Engeln: Am. Jour. Sci. (4) **40,** 464 (1915).

[2] Pollock and Collier: Nature, **31,** 216; Osmond: Ibid. **31,** 532 (1885); McConnel: Phil. Mag. (5) **29,** 461 (1890).

angles. The rate of growth varies with the density of fog and the speed of the wind. A rough average is half an inch per hour and two inches per hour seems to be a maximum value. The phenomenon is what one would expect from liquid particles cooled below the freezing point. The same thing occurs on Mount Washington where the crystals are known as frost feathers,[1] though they are not considered as resulting from supercooled fogs. On Mount Washington the frost feathers are formed only when the wind is northerly. With a southerly wind, masses of greenish-blue ice are formed, especially on the telegraph poles.

These supercooled fogs are quite different from the so-called ice storms which occur once or more every winter and which sometimes do so much damage to trees. In the ice storms the moisture deposits as liquid water on the branches and twigs, freezing there to solid ice. These storms occur when the temperature is below freezing and a warm rain or mist comes down from above without getting chilled to the freezing point before it strikes the trees.

The optical properties of suspended drops of water are very interesting, the best known case of this being the rainbow.[2] When the sun is shining on fog or mist, a fog bow[3] is often seen differing considerably in appearance from the ordinary rainbow—far broader and, though quite bright, nearly colorless. The size of the bow depends on the size of the drops, the diameter of the bow being less with very small drops[4] than with large drops. Horizontal rainbows are often seen when the surface of a lake is covered with minute drops of liquid.[5]

Under suitable circumstances we may see coronas surrounding the sun or the moon.[6] They are due to the interposition of small spherules of water, which act the part of diffracting obstacles. In order to have the formation of a well-defined corona, it is essential that the particles be exclusively or preponderatingly of one size. By measurements of coronas it is possible to infer the

[1] Mount Washington in Winter, 285 (1871).

[2] Moore: Descriptive Meteorology, 249 (1910).

[3] McConnel: Phil. Mag. (5) **29,** 453 (1890).

[4] Wood: Physical Optics, 346 (1911).

[5] Juday: U. S. Monthly Weather Review, **44,** 65 (1916); Nakamura: Jour. Meteorological Soc. Japan, **36,** 1; Otobe: Ibid. **36,** 3, 7 (1917).

[6] Encyclopædia Britannica, 11th Ed. **8,** 244 (1910).

size of the particles to which they are due, an application of considerable interest in the case of natural coronas, the general rule being that the corona is larger the smaller the water particles. Young employed this method not only to determine the diameters of cloud particles (*e.g.*, 1/1000 inch); but also those of fibrous materials for which the theory is analogous.

Every one is familiar with the colored coronas surrounding bright objects, as seen through a pair of spectacles freshly bedewed with moisture. These colors are due to optical interference and are entirely analogous to those seen through a fog. Such circles may be seen around the sun almost any day of the year if we view it by reflection from some poorly reflecting surface, like water, in order to eliminate the blinding glare of the sunshine. In the case of the largest corona, known as Bishop's Ring, the average diameter of the particles[1] of this ring by diffraction was calculated to be about 0.00015 of an inch (about 4μ).

The production of coronas in the laboratory was observed by Coulier in the paper referred to and has been the subject of study for many years by Barus.[2] To get the best effects the drops should be uniform in size.

Piazzi Smyth[3] reports that for several days in India and elsewhere the disc of the sun was blue or green in the morning and evening. He considers that this was due to a high concentration of water vapor which cut out the red end of the spectrum; but this does not seem to be an absolutely satisfactory explanation.

The brilliant sunset and sunrise colors are due in part to the presence of suspended particles of water.[4] In the lower half of the atmosphere there are frequently larger particles, probably of aqueous vapor, dust, and smoke that scatter the blue and transmit the red, so that after sunset or before sunrise beams of reddish light permeate the atmosphere above our heads.

While fog is due to the production of very small drops, rain is due to the formation of larger drops which fall with perceptible

[1] These were solid particles; but formed a corona and not a halo. A corona is due to diffraction and is red on the outside. A halo is due to refraction and is red on the inside.

[2] Smithsonian Inst., **29,** No. 13 (1909); Carnegie Inst. Pub. No. 62 (1907); No. 96 (1908).

[3] Trans. Roy. Soc. Edin., **32,** 389 (1884).

[4] Moore: Descriptive Meteorology, 245, 255 (1910).

speed. There is no absolute dividing line between the two because most people would classify as rain what a Scotchman might call a mist. According to the Weather Bureau, rain appears[1] to begin when the drops reach a diameter of 0.04 mm. The maximum rate of fall of these drops is very small. Larger drops fall faster. According to Lenard[2] drops of 1.28 mm diameter have a final velocity of 4.8 meters per second, those with a diameter of 3.49 mm reach a velocity of 7.37 meters per second, while drops from 4.50–6.36 mm show a practically constant rate of about 8 meters per second. This limiting value is due to the drops becoming deformed, so that they become flattened out, instead of retaining the shape of spheres. They therefore offer an increased resistance to the air through which they fall. In consequence of this deformation large drops break up rapidly in the air into smaller drops. Lenard found that drops of 4 mm diameter were stable under all conditions, but that drops of 5.5 mm diameter and over could not exist for more than a few seconds after attaining their final velocity relatively to the air. This is in harmony with the results of other observers. Wiesner[3] concluded that natural rain drops cannot have a diameter larger than 7.2 mm, while Ritter found that the largest drops of natural rain did not exceed 6.6 mm diameter. An independent confirmation is found in Bentley's experiments on the size and frequency of drops during rains in northern Vermont. His data are given in Table LI.

TABLE LI.—MEASUREMENTS OF DIAMETERS AND FREQUENCIES OF RAIN DROPS

Apparent size	Diameter of drops in mm	Frequency of drops	
		No. observed	Percent
Very small	Under 0.8	149	17
Small	0.8–1.5	288	34
Medium	1.6–3.5	254	29
Large	3.4–5.0	141	16
Very large	Over 5.0		

[1] MOORE: Descriptive Meteorology, 205 (1910).

[2] Met. Zeit., **21**, 249 (1904).

[3] MOORE: Descriptive Meteorology, 208 (1910).

It is possible that the very smallest drops often escaped observation and that the percentage of very small drops should be more than 17. In any case the mean diameter is not over 1.5 mm and the instructive thing is to see the very small percentage of drops larger than 5.0 mm diameter.

Simpson[1] has recently developed a very interesting theory in regard to thunderstorms. He considers the case of a rapidly ascending current of air which spreads out and slows up above a certain height. Large rain drops will fall through this air current until they reach a point where they are broken into smaller drops and are then carried to the upper and colder levels where they grow again and repeat the cycle. When the drops break up they become charged positively, while the negative ions are carried up more rapidly by the air and are finally caught by cloud particles at some higher level. On this hypothesis positively charged rain should fall in bursts in the center of the thunderstorm while negatively charged rain should fall in the lulls and on the outskirts of the thunderstorm. This actually happens. Simpson satisfied himself that the electricity generated by the breaking up of the falling drops might easily account for the gradient of 30,000 volts/cm necessary for lightning. No calculations were made by Simpson as to the possibility of duplicating these phenomena in the laboratory by a vertical blower. If it were feasible to have a synthetic thunderstorm, this would be of great value in the study of meteorological phenomena.

It is interesting to note that while drops become charged positively on splashing, water vapor condenses more readily on negative ions[2] than on positive ones and that liquid drops take up negative ions more readily than positive ones.[3]

The precipitation of a fog or mist is an important problem; but can best be taken up in connection with the precipitation of smoke or dust because the technical methods are as yet the same in the two cases. Reference may, however, be made here to a process devised by Pelouze and Audouin,[4] who force the mist

[1] Phil. Trans., **209A,** 379 (1909); Humphreys: Jour. Franklin Inst., **178,** 751 (1914); Phys. Rev. (2), **6,** 516 (1915).

[2] Wilson: Proc. Roy. Soc., **64,** 127 (1898).

[3] Schmauss: Drude's Ann., **9,** 224 (1902); Seeliger: Ibid., **31,** 510; 33, 451 (1910); Lenhardt: Ibid., 42, 45 (1913).

[4] Moore: Descriptive Meteorology, 205 (1910).

through a series of small apertures and cause the streams to impinge on a flat surface placed opposite. They consider that by this means the drops are brought into contact with one another and therefore coalesce to larger drops, which latter adhere to the surface against which they are driven. The method has been used for the separation of tar, carbon bisulphide, etc., from coal gas. It is interesting as being the mechanical analogue of the Cottrell electrical method.

Smoke

As an intermediate step between fog and smoke we have the precipitation of water vapor in solid form as snow, sleet or hail. When the dew point is decidedly below freezing,[1] water vapor condenses directly to crystals of ice, ice needles, or snow flakes. When supercooled rain drops strike solid substances they cover these with a coating of transparent ice. When snow crystals and supercooled rain drops come in contact we get sleet, and sleet changes to hail when the supercooled drops precipitate in the form of sheaths of ice. In order that hail stones should grow to any appreciable size, they must be carried up and down a number of times. Even in midsummer the temperatures six kilometers above the earth's surface will be at least $-26°$ and may easily be $-40°$. The reason that we get hail chiefly in summer is because then we have the hot air of the earth's surface giving a sharp temperature gradient and therefore a rapid upward sweep. The warm air may contain a great deal of water vapor which permits the precipitation of large amounts of ice. In winter the vertical temperature gradient is less and also the amount of water vapor in the air. Consequently we get no real hail, especially far from the sea.

Hail stones[2] can only form if they are supported during formation by strong ascending currents. Further, the structure of a hail stone indicates that it is often carried up and down past the zero isothermal. Now a current of air sufficiently strong just to support a hail stone as big as a pea would be more than sufficient to carry up the water it condenses within itself; hence hail stones would always have a greater downward velocity relative

[1] Moore: Descriptive Meteorology, 205 (1910).

[2] Simpson: Phil. Trans., **209A**, 412 (1909).

to the ascending current than the water in the current and there would be a large amount of splashing between the two. There would be, consequently, a much greater amount of separation of electricity than would have taken place without the hail stones, and this might very well account for the great violence of the electrical discharges in hail storms.

Tolman[1] and others have devised a form of ultramicroscope which they call a Tyndallmeter for the quantitative study of smokes and have determined the relation between the intensity of the Tyndall beam and the size of the particle, making use also of silica suspensions as standards. It has been shown by Lord Rayleigh on theoretical grounds that, when the particles are very small compared with the wave-length of light, the intensity of the Tyndall beam should be proportional to the number of particles per unit volume and to the sixth power of their diameter. For larger particles Tolman considers that the intensity would be proportional to the area of reflecting surface, in other words to the square of the diameter. If we define the concentration, C, as the mass per unit volume irrespective of the number of particles, we get two equations:

$$T = RCd^3 \text{ for very small particles.}$$
$$T = R_1C/d \text{ for large particles.}$$

For very small particles, the Tyndallmeter reading, T, will increase with increasing diameter, whereas it will decrease for large particles. The results show that, in general, increased subdivision means an increased Tyndallmeter reading. The observations of Mecklenburg[2] on sulphur suspensions agree well with Rayleigh's formula for diameters from 5–840$\mu\mu$; whereas some of the smokes show the opposite result for particles smaller than the largest of these. Mecklenburg's work will have to be repeated before the discrepancy can be explained.

Unless subjected to special treatment, the air always contains dust. The air of large cities invariably shows hundreds of thousands of dust-motes per cubic centimeter,[3] that of the village or town thousands, and that of the open country at least hundreds.

[1] Jour. Am. Chem. Soc., **41**, 297, 300, 304, 575 (1919).
[2] Zeit. Kolloidchemie, **16**, 97 (1915).
[3] Moore: Descriptive Meteorology, 30 (1910).

The dust may be soil[1] from the fields and roads, particles of animal or plant origin, including pollen, products of combustion, salt from the spray of the ocean, volcanic dust, or cosmic dust. The dust from the eruption of Krakatoa was shot high into the air and was carried entirely round the world, falling on the decks of ships and on various parts of the earth. Owing to the enormous distances to which volcanic dust may be carried, it is necessary to have some definite test before we can say that a given sample of dust is really cosmic dust coming from meteors which have burned up in passing through the earth's atmosphere. This matter has been studied by Hartley and Ramage,[2] who collected numerous samples of dust in the neighborhood of Dublin and examined them spectroscopically as well as other samples furnished by friends.[3] "The specimens of soot required no preliminary treatment before being burnt, and the analysis of each is given in the tabular statement only; but the different kinds of volcanic dust and flue dust were dissolved and the silica removed, after which the bases were separated into groups, and the spectra of the groups photographed." The data for the bases are given in Table LII, italics being used when only a trace of the metal is present. The relative strength of the lines, as seen by comparing the different spectra, is, in some instances, indicated in the table by suffixes, the number 1 indicating the weakest line and 10 the strongest.

Hartley and Ramage drew the following conclusions:

(1) The presence of nickel, as shown by the examination of soot, is not positive evidence that the dust from the clouds comes from other than a terrestrial source.

(2) The dust which fell on the 16th and 17th of November, 1897, with its regularity in composition and its similarity to meteorites, being magnetic, also its comparative freedom from extraneous matter, exhibits properties which are quite in favor of its cosmic origin. Moreover, its composition is totally unlike that of volcanic dust and flue dust from various chemical and metallurgical works. This dust for the most part fell on a perfectly

[1] See Ehrenberg: Die Bodenkolloide, 209 (1915).

[2] Proc. Roy. Soc., **68,** 97 (1901).

[3] Data on the composition of soot have been published recently by Cohen and Ruston: Jour. Soc. Chem. Ind., **32,** 1360 (1911).

TABLE LII.—COMPOSITION OF DUST FROM THE AIR

	Na	K	Rb	Cu	Ag	Mg	Ca	Sr	Ga	In	Tl	Fe	Ni	Mn	Cr	Pb
Dust from sleet fell March 28, 1896	Na	K	Rb?	Cu	Ag		Ca		Ga		Tl	Fe	Ni	Mn		Pb
Dust from hail fell April 14, 1897	Na	K		Cu	Ag		Ca		Ga?			Fe	Ni	*Mn*		Pb
Dust from clouds fell Nov. 16, 1897	Na	K		Cu	Ag		Ca		Ga		Tl	Fe	Ni	Mn	*Cr*	Pb
Dust from rain fell Nov. 13–15, 1897	Na	K		Cu	Ag		Ca	*Sr*	*Ga*		Tl	Fe	Ni	*Mn*		Pb
Volcanic dust from New Zealand:																
(1) Te Ariki	Na	K	Rb	Cu	*Ag*	MgO	Ca	Sr	*Ga*			Fe	*Ni*	Mn		Pb
(2) Tauranga	Na	K	Rb	Cu	*Ag*	MgO	Ca	Sr	*Ga*			Fe	*Ni*	Mn		Pb
(3) Te Hope-O-Toroa	Na	K	Rb	Cu	*Ag*	MgO	Ca	Sr	*Ga*			Fe	*Ni*	Mn		Pb
Pumice from Krakatoa	Na	K	Rb	Cu	Ag		Ca	Sr	Ga	In?		Fe	Ni	Mn		Pb
Lead chloride from crater of Vesuvius	Na	K	Rb	Cu							Tl	Fe				Pb
Soot from chimneys:																
(1) Bedroom chimney	Na_9	K_1	Rb?	Cu_2			Ca_7	*Sr*	Ga_2		Tl_1	Fe_8	Ni_1	Mn_1		Pb_4
(2) Kitchen chimney	Na_3						Ca_3					Fe_2				
(3) Laundry chimney	Na_9	K_4	*Rb*?	Cu_4	*Ag*		Ca_7	Sr_1	Ga_2		Tl_2	Fe_9	Ni_3	Mn_3	Cr_1	Pb_5
(4) Assay laboratory, fusion furnace	Na_7	K_8	*Rb*?	Cu_4	Ag_4		Ca_2		Ga_2		Tl_3	Fe_7	Ni_3	Mn_1		Pb_9
(5) Assay laboratory, gas muffle	Na_7	K_3		Cu_3	Ag_2		Ca_3		*Ga*?		Tl_1	Fe_7		Mn_1		Pb_8
(6) Heating apparatus, furnace	Na_9	K_4	Rb?	Cu_3			Ca_9	Sr_2	Ga?		Tl_1	Fe_9	Ni_1	Mn_6		Pb_3
Flue dust:[1]																
(1) Gas works, Crewe	Na	K	*Rb*?	Cu	Ag		Ca	Sr	Ga			Fe	Ni	Mn		Pb
(2) Boyd's chemical works, Dublin	Na	K		Cu	Ag		Ca			In	Tl	Fe				Pb
(3) Nicholson's copper works, Leeds, 0.5 g	Na	K	Rb	Cu	Ag		Ca		Ga	In	Tl	Fe				Pb
Ditto, 20 g[2]	Na	K	Rb	Cu	Ag		Ca	Sr	Ga	In	Tl	Fe	Ni	Mn	Cr_1	Pb
(4) Ferromanganese furnace, Pittsburgh	Na	K	Rb	Cu			Ca				Tl	Fe	Ni	Mn		Pb
(5) Ferromanganese furnace[3]	Na	K	Rb	Cu	Ag		Ca		Ga	*In*	Tl	Fe		Mn		Pb
(6) Cleveland iron furnace, Samuelson, Middlesborough	Na	K	Rb	*Cu*	*Ag*		Ca		*Ga*		Tl	Fe	*Ni*	Mn		Pb
(7) Cleveland iron furnace	Na	K	Rb	*Cu*	*Ag*		Ca		*Ga*	*In*	Tl	Fe	*Ni*	Mn		Pb
(8) Basic iron furnace[3]	Na	K	Rb	*Cu*	*Ag*		Ca	Sr	*Ga*	*In*	Tl	Fe	*Ni*	Mn		Pb
(9) South Wales iron furnace	Na	K	Rb	*Cu*	*Ag*		Ca		*Ga*	*In*		Fe				Pb
Meteoric stone, Alfianello	Na	K		Cu	Ag	MgO	Ca		*Ga*			Fe	Ni	Mn		Pb
Meteoric stone, Pultush	Na	K		Cu	Ag	MgO	Ca					Fe	Ni	Mn	Cr	Pb
Meteoric stone, Moos	Na	K		Cu	Ag	MgO	Ca	*Sr*				Fe	Ni	Mn	Cr	Pb
Siderolite Atacama	Na	K		Cu	Ag	MgO	Ca					Ge	Ni	Mn	Cr	Pb

[1] Lithium was found in all the flue dusts.
[2] Bi, Al, Zn, Cd, Sn, *Cs* and *Co* were found in this dust.
[3] *Cs* was found in this dust.

calm fine night, and there was no rain for twenty-four hours or more afterwards.

"We beg to draw attention once more to the very wide distribution of gallium in minute proportions; it occurs in all aluminous minerals, flue dust of every kind, soot and atmospheric dust, also in a great variety of iron ores. Bauxite contains it in larger proportion than any other mineral, but the quantity even in this substance is very small. We have hopes of finding it concentrated in some mineral, as thallium, caesium, germanium, and indium are. Indium and thallium, the other members of the same group of elements, are found in blende and pyrites, and accordingly we might expect gallium to occur in a concentrated state in a sulphide, arsenite, or similar compound. Judging, however, from its analogy with aluminum, there does not seem to be much probability of this."

Unfortunately Hartley and Ramage do not tell us exactly how to identify cosmic dust and it is not an easy matter to formulate a rule from the data. The first four samples of dust differ from the volcanic dust in not containing magnesia or strontium; they differ from the flue dust and the soot from chimneys in not containing rubidium and in containing more nickel. If we are to take only the dust which fell on November 16 and 17, 1897, as of cosmic origin, the only difference is the trace of chromium. The situation is complicated farther by the fact that the meteoric stones all contain magnesia and chromium. It is not clear at all why these should have disappeared in the alleged cosmic dust. So far as one can formulate a conclusion from this work, it seems to be that dust is of cosmic origin when it contains sodium, potassium, copper, silver, calcium, gallium, thallium, iron, nickel, manganese, chromium, and lead; but no rubidium, strontium or magnesia. The dust must also be magnetic, this last probably being the most important criterion of all though it does not appear in the table.

Preliminary work on the precipitation of smoke and dust was done by Nahrwold[1] and by Aitken,[2] the latter of whom showed that tobacco smoke could be precipitated quantitatively by passing it through a hot-cold tube, the smoke condensing on the cold

[1] Wied. Ann., **5**, 460 (1878).

[2] Nature, **29**, 322 (1884); Trans. Roy. Soc. Edin., **32**, 239 (1884).

tube. The film of condensed air round the particles has a lower surface tension on the hot side than on the cold side and consequently flows round the particles from the cold side to the hot side, causing the particles to move in the opposie dirtection or along the gradient of falling temperature. The temperature gradient has to be pretty steep to produce a marked effect, say 100°/cm, so that the method has never been developed as a practical means of removing smoke. A slight movement has been observed by Wells and Gerke[1] due to the heat from the source of light used in the ultramicroscopic examination of smokes.

Lodge[2] tried the effect of electrification on a mass of smoke. With potentials of one hundred volts very little effect could be detected. When the potential rose to a few thousand volts and a brush discharge began to be possible, the smoke agglomerated and settled very rapidly. The theory of this has never been worked out. In ordinary smokes about 30 percent of the particles are charged electrically. It may be that the alternating current reverses the sign of the charge periodically and that the particles agglomerate when they are electrically neutral or it may be that it causes the charged particles to collide with the uncharged ones. In connection with this it would be interesting to determine the effect of a high-voltage alternating current on the stability of a suspension in a practically non-conducting liquid.

The general principle of electrical precipitation of suspended particles was patented by A. O. Walker of the Dee Bank Lead Works. In 1885 an apparatus was installed consisting of a system of metallic points situated in the flue from the lead furnaces and excited from two Wimshurst machines with glass plates five feet in diameter, each machine being driven by a one-horse power steam engine. The process seems not to have been a commercial success. It is only through the work of Cottrell[3] that the electrical precipitation of suspended particles has been put on a commercial basis. Cottrell believed that in the case of the large volumes of rapidly moving gases in smelter flues the agglomerating and settling process was too slow even though the flues were expanded into as large dust chambers as were commercially

[1] Jour. Am. Chem. Soc., **41,** 325 (1919).
[2] Phil. Mag. (3), **17,** 214 (1884); Jour. Soc. Chem. Ind., **5,** 572 (1886).
[3] Jour. Ind. Eng. Chem., **3,** 542 (1911).

feasible. It is in such cases that direct current methods have been particularly important.

If a needle point is connected to one side of a high potential direct current line opposite to a flat plate connected to the other side of the line the air space between becomes highly charged with electricity of the same sign as the needle point, irrespective of whether this is positive or negative, and any insulated body brought into this space instantly receives a charge of the same sign. If this body is free to move, as in the case of a floating particle, it will be attracted to the plate of opposite charge and will move at a rate proportional to its charge and the potential between the point and the plate. Even if there are no suspended particles the gas molecules themselves undergo this same process, as is evidenced by a strong wind from the point to the plate even in perfectly transparent gases. The old familiar experiment of blowing out a candle flame by presenting it to a charged point, is simply another illustration of the same phenomena.

The procedure actually used to get direct current consisted in transforming the alternating current from an ordinary lighting or power circuit up to some 20,000 or 30,000 volts and then commutating this high potential current into an intermittent direct current by means of a special rotary contact maker driven by a synchronous motor. This direct current is applied to a system of electrodes in the flue carrying the gases to be treated. While any smooth conducting surface worked well for the plate electrodes, it was difficult to find anything suitable for the point electrodes when working on a commercial scale. The problem was solved by using asbestos or mica, the fine filaments of the one and the scales of the other supplying the discharge points or the edges of the excessive fineness required. These materials are twisted up with wires or otherwise fastened to suitable metallic supports to form the discharge electrodes in such wise that the current has to pass only a short distance by surface leakage over them, the slight deposit of moisture or acid fume, naturally settling on them, serving to effect the conduction. If the condition of the gases does not supply such coating sufficiently, a special treatment of the material before being placed in the flue is resorted to.

The process was installed successfully at the contact sulphuric

acid plant of the Hercules Works of the E. I. du Pont de Nemours Powder Company at Pinole on San Francisco Bay; at the refining plant and at the pyrites and matte roasters of the Selby Smelting and Lead Company; and at the Balaklala smelter.

In the case of smelting plants the process is not a universal panacea because it does not remove gases and the farmers object to sulphur dioxide about as much as they do to sulphuric acid, arsenic, etc. In cases where suspended solids are the only source of trouble, the process is capable of eliminating the whole trouble. This was shown at Riverside in California, where there is a cement plant in the neighborhood of orange groves and the dust of course settles on the leaves.[1] A rotary kiln 100 feet long and 7 feet in diameter, oil-fired, will yield about 50,000 cubic feet of stack gases per minute. The gases above the combustion zone in the stack have a temperature of 450°C. and carry dust aggregating between four and five tons per twenty-four hours. With these dry gases it was possible to use steel construction without cooling the gases. The installation was placed at the top of the stacks 80 feet up. It is probable that a considerable portion of the needs of the country for potash can be met by utilizing the dust from the cement plants.

In the Washoe reduction works of the Anaconda Copper Mining Company the Cottrell process has been introduced on so large a scale[2] that the point electrodes consist of one hundred and eleven miles of chains.

The Cottrell process has proved a great success commercially and new uses for it are continually being found. A modification of the apparatus has recently been made for the study of toxic smokes in the laboratory.[3] The apparatus consisted essentially of a central wire cathode surrounded by a cylindrical anode of aluminum foil 0.001 inch in thickness. An alternating current running up to 15,000 volts was rectified by means of a General Electrical Company "Kenotron." Complete precipitation could be obtained even when smoke was drawn through the apparatus at a rate of about five liters per minute. The anode

[1] SCHMIDT: Jour. Ind. Eng. Chem., **4,** 719 (1912).

[2] CHANDLER: Jour. Ind. Eng. Chem. **11,** 138 (1919).

[3] TOLMAN, REYERSON, BROOKS and SMYTH: Jour. Am. Chem., Soc., **41,** 587 (1919).

could be removed and weighed, thus giving a satisfactory method of determining the concentration of any smoke. Examination of the precipitate microscopically makes it possible to tell whether one is really dealing with a smoke or with a fog.

When dust is blown about by the wind, it becoms electrified.[1] In South Africa at Bloemfontein at an elevation of 4500 feet, the normal fine weather charge of the air is positive and seldom exceeds a maximum value of 200 volts per meter. During a dust storm the sign of the charge changes and the value may exceed 500 volts per meter. A so-called dust devil or whirlwind which carries a column of fine sand up two or three hundred feet in the air will affect an instrument two miles away, reversing the charge. This is because the sand particles are charged positively. In England a cloud of dust increases the positive charge in the air instead of decreasing it. This is because the dust in England is usually calcareous and acquires a negative charge. It is also known that red lead acquires a positive charge when blown into the air and sulphur a negative one.

From the experiments that he made, Rudge deduced four generalizations.[2] Non-metallic elements give positively charged clouds when the finely-divided solid material is blown into a cloud by a current of air. Metallic elements give negatively charged clouds when the finely divided material is blown into a cloud by a current of air. Solid acid-forming oxides give positively charged clouds, and basic oxides negatively charged clouds. In the case of salts the charge apparently depends on the relative strength of adsorption of positive and negative ions. The whole subject of frictional electricity should be gone over from the viewpoint of adsorption of ions. If this were done, it would undoubtedly bring some order out of the present chaos. Guttmann[3] gives some data on electrical disturbances in powder mills.

I am indebted to Dr. Reid Hunt for information in regard to another difference between siliceous and calcareous dusts. The flint pariclte in South Africa are not rounded and the sharp edges of the dust wound the lungs and permit the tuberculosis bacteria to enter, whereas there is not the same danger in the

[1] Rudge: Phil. Mag. (6), **23,** 852 (1912); **25,** 481 (1913).
[2] Cf. Knoblauch: Zeit. phys. Chem., **39,** 225 (1902).
[3] Jour. Soc. Chem. Ind., **8,** 60 (1889).

case of calcareous dusts. If dried rhubarb is ground up, the calcium oxalate forms a dust composed of needles exceedingly irritating to the lungs.

The optical phenomena due to suspended solids are quite as interesitng as those due to suspended drops of liquid. The Tyndall effect, or the scattering of a convergent or parallel beam by suspended particles, has been referred to in connection with the ultramicroscope; and in the discussion of the color of colloids it was pointed out that the blue color of skimmed milk is due to the fact that the blue rays are scattered more than the red. The blue of cigar smoke is a similar phenomenon and Lord Rayleigh[1] has shown that the blue of the sky can be accounted for very well as due to scattering by particles of water, ice, or dust. He even claims that the molecules of oxygen and nitrogen are large enough in themselves to give rise to a blue sky even if the air contained no suspended matter in the ordinary sense of the word. From his formula he deduces the value of the Avogadro constant, the number of molecules per gram molecule.[2] Without being able to point to any error in Lord Rayleigh's mahtematics, it seems to me that his assumption in regard to the behavior of oxygen and nitrogen molecules is probably wrong. The molecular weight of oxygen is so low that practically all solutions and gaseous mixtures would be blue by reflecetd light and red by transmitted light if Rayleigh were right.

Nichols[3] is by no means certain that one can account quanittatively for all the phenomena of the blue sky on the basis of solid or liquid particles. The distribution of intensities seems not to be exactly that required by Rayleigh's formula. The best explanation of the discrepancy is either that the air itself absorbs blue to some extent or that some variable constituent of the air does, such as ozone, for instance.

Many of the color effects in the sky apart from the blue are due to the presence of solids. Moore[4] says that if it were not for dust-motes there would be a different and less brilliant twilight. The bending or refraction of light, as the sun's rays pass obliquely

[1] Phil. Mag. (4) **41,** 107, 274, 447 (1877); (5) **12,** 81 (1881); **47,** 375 (1899).
[2] Cf. PERRIN: Die Atome, 129 (1914).
[3] Phys. Rev., **26,** 497 (1908).
[4] Descriptive Meteorology, 32, 254, 245 (1910).

from the ether, at sunrise, or at sunset, into the optically denser medium of the air, displaces the apparent position of the sun, elevating it by an amount about equal to its apparent diameter, so that one may still see it and receive its light directly when geometrically it is entirely below the horizon. A little later in the evening and its rays fall upon the upper air too obliquely to be bent down to the earth by refraction, but darkness does not yet ensue, for the rays are scattered by the molecules of gases and the dust-motes and sent downward from particle to particle, resulting in a soft shimmering light that fades away almost imperceptibly, and which may last for hours in higher latitudes, because of the obliqueness there of the sun's path to the horizon.

When the harmattan blows on the west coast of Africa, the sky has a chalky-white tint and the air is very dry. The whitish tint is due to the presence of innumerable fragments of microscopic diatoms or siliceous shells. The whitish color of the haze must be attributed to the reflection of light from their surfaces. A similar white haze occurs in air that is full of grains of pollen or fine crystals of snow, or almost any other kind of small particles.

"An unusual illustration of selective absorption was given on the occasion of the most violent volcanic eruption of historic times—that of Krakatoa—on August 27, 1883, when an immense volume of dust and aqueous vapor was thrown to a great height in the atmosphere above the Straits of Sunda. The antitrades spread this over the northern hemisphere, and winds higher up in the tropics carried it westward round the world and formed a layer of from 5 to 15 miles above the earth's surface, consisting undoubtedly of minute particles. After sunset, and by virtue of the diffusion of red light by this layer of particles, the whole western sky, even to near the zenith, glared with a lurid red as though lighted up from some great and distant fire. These remarkable sunsets continued, diminishing slowly in brilliance, through the years 1884 and 1885 in temperate latitudes, while their northern limit advanced slowly toward the pole, showing that minute particles of solid matter may float for years in the high upper atmosphere, so long as slowly rising currents buoy them up. Isolated clouds of such material may always be floating in the upper atmosphere and may give rise to the noctilucent or night-shining clouds that are occasionally observed at

great altitudes when the observer looks northward in midsummer."

The tails of comets seem to consist almost entirely of colloidal particles.[1] The great comet of 1882 was invisible against the solar disc, a position which corresponds to attempted observation of colloidal particles in the ordinary microscope against a luminous background. It became visible again after passing beyond the sun's disc, a position correspondng to successful observation of the same colloidal particles in the ultramicroscope against a dark background, the eye of the observer being protected from the source of illumination. The streaming of the tail of a comet away from the sun may be due to the ionization of the colloidal particles, and their consequent electrical repulsion, it may be a thermal effect, or it may be due to the pressure of light as was pointed out by Maxwell. The intensity of the action of the sun's rays on a particle depends on its surface which varies as the square of the diameter, while the force of gravity tending to carry the particle to the sun is proportional to the mass of the particle and this varies as the cube of the diameter. In the case of a particle having a density equal to water the repulsion should balance the gravitational effect[2] when the diameter is 1.5μ and when it is $70\mu\mu$. For particles of greater density a balance would be reached at a still greater degree of dispersity.

In the very clear air of Egypt the contrast between lights and shadows is very marked because the shadows are illuminated but slightly by diffracted light and are therefore darker than in countries where there is more dust or moisture. If one is to get any detail in the shadows, one must expose a negative about twice as long[3] as one would in northern latitudes under equally favorable conditions. Luckiesh[4] points out that a slight haze increases the brightness of the sky very much.

Aitken[5] has shown that water vapor in itself does not produce any effect of haze, that haze is due entirely to dust, and that the

[1] Alexander: Colloid Chemistry, 37 (1919).

[2] Encyclopedia Britannica, 11th Ed., **6,** 761 (1910).

[3] Beck: Jahrbuch der Photographie, **18,** 159 (1904); Phot. Correspondenz, **1989,** 45.

[4] Jour. Franklin Inst., **187,** 295 (1919).

[5] Encyclopedia Britannica, 11th Ed., **8,** 715 (1910).

density of the haze increases with the number of the dust particles in the air and also with the relative humidity. In Table LIII are given Aitken's results as to the number of particles of atmospheric dust in a column of air having a cross-section of one square centimeter required to produce a complete haze, that is, to make a distant object invisible. The figures are of course not dependent on the length of the column.

TABLE LIII.—PRODUCTION OF COMPLETE HAZE

Wet-bulb depressions	Number of particles to produce a complete haze
2° to 4°	12,500,000,000
4° to 7°	17,100,000,000
7° to 10°	22,600,000,000

The whole effect of light on fog and haze may change in a remarkable way if one varies the ratio between polarized and unpolarized light as has been brought out clearly by Tyndall.[1] The light of the sky is polarized and may be quenched in great part by a Nicol prism while the light from a cloud is not polarized and therefore cannot be extinguished. A cloud may appear to the naked eye dark against a bright sky and yet appear as a white cloud on a dark ground if the light from the sky is quenched by means of a Nicol prism. In the same way the effect of haze may be overcome and a mountain may be seen clearly when using a Nicol prism even though almost invisible to the naked eye. The elimination of polarized light in this way was made use of during the war to detect camouflaged ships and periscopes. Still better results were obtained with a Savart plate, the lines disappearing where the ship was.

With ice crystals in the air, we sometimes get halos and mock suns.[2] The reflection and refraction of the sunlight by small ice crystals in the air give rise to a very complicated series of phenomena, which unlike the rainbow, can be seen at all altitudes of the sun. The ice crystals are all hexagonal, either flat plates or

[1] Fragments of Science: The Sky of the Alps.

[2] WOOD: Physical Optics, 347 (1911); MOORE: Descriptive Meteorology, 250 (1910).

needles (spiculæ). In still air these crystals will fall slowly with the principal axis vertical in the case of the flat plates or with the principal axis horizontal in the case of spiculæ, because bodies moving through a resisting medium set themselves in the position of greatest resistance. It is possible to show that the observer, looking through a filmy cloud of such crystals, would see in one part of the sky a halo, in another part an arc of light, and in other directions bright spots like the sun, all of them arranged symmetrically with regard to the sun and the observer's zenith. This resulting complex arrangement of circles and spots is known as a complete halo. It is rare that all possible combination are seen at any one time, but on several occasions solar halos have been recorded that corresponded very nearly to this ideal.

The removal of dust from the air is an important matter in some industries. In photographic work dust particles in the film mean clear spots on the negative and black ones on the positive. In the manufacture of gas mantles, contamination by dust may cause pinholes in the product. Dust and soot in the air may be a very serious matter in the ventilating of electrical generators because 65,000 cubic feet of air may pass through a moderately large generator per minute or about 94,000,000 cubic feet per day. There are a number of firms which make apparatus for washing and cooling air. All of them remove the dust by spraying drops of water through the air instead of bubbling air through the water, this latter method not being effective.[1] Everybody knows how effectively a rain clears the air and it is this principle which is employed commercially.

The question of flames is one of colloid chemistry. A flame is a reacting gas and the luminosity is due either to incandescent solid particles or to chemical reactions. The luminosity of ordinary flames is due chiefly to incandescent particles of carbon, the presence of which can be shown by pressing a cooled dish down upon the flame, when a precipitate of carbon is formed. In the case of flames colored by salts, the luminescence is due chiefly to chemical reactions.[2] In the green cupric chloride

[1] See however Hurter: Jour. Soc. Chem. Ind., **4**, 639 (1885); **6**, 707 (1887); **12**, 227 (1893).

[2] Weiser: Jour. Phys. Chem., **18**, 281, 762 (1914); **19**, 310 (1915).

flame, for instance, the cupric chloride dissociates temporarily into copper and chlorine, the light being due to the recombination. The presence of free copper in the flame can be shown by placing in it a porcelain tube through which cold water flows. Metallic copper is precipitated as a metallic mirror on the cold portion of the tube. Nearly all the metals can be precipitated similarly from flames containing their salts, though in some cases the temperature of the oxyhydrogen flame is necessary for a satisfactory dissociation.

If the smoke particles are concentrated enough to form a cloud which moves along, they will tend to carry with them the gases inside the cloud because the mingling with the air takes place relatively slowly by diffusion. At the eruption of Mont Pelée when St. Pierre was destroyed, the descending cloud carried down with it large amounts of heated steam. The mean density of the water vapor and the solid particles was greater than that of air and the cloud sank as a whole. In the late war the French always mixed some form of smoke with their gas clouds. That had several advantages. It enabled the observers to see what the gunners were doing, it increased the apparent density of the cloud, and it caused the cloud to hold together better than it would have otherwise. It is only fair to say, however, that there are no satisfactory data to show how real these last two advantages are; but one would expect them to be of less importance in gas warfare where the amount of smoke is small than in the case of a volcanic eruption where the total amount of solid matter in the cloud is relatively high. On the other hand a smoke cloud may hold together pretty well for a mile or two, which it could hardly do if the air in the cloud did not move with it to a great extent.

Garcia de la Cruz[1] found that a hydrogen-filled balloon could be adjusted so that it would sink in pure air and would rise in air containing any kind of smoke.

Precipitation of Solid

There seems to have been no systematic study of the effect of conditions on the form in which a solid precipitates from a gas

[1] Spring: Mem. Soc. belge Geologie, **17,** 30 (1903).

or vapor, although there are a good many scattered observations. With carbon the matter is important, in its bearing on the production of lamp-black, charcoal, coke and metallized filaments. Monier[1] states that carbon made from pure sugar is very hard and will scratch topaz though not corundum. Schützenberger[2] reports that when cyanogen is passed over carbon soaked with cryolite and heated to a cherry-red heat, it decomposes into nitrogen and filamentous carbon. Constant and Pélabon[3] have also made observations on filamentous carbon. Love[4] reports on the carbon deposits obtained in gas burners. Luzi[5] obtained a silvery graphite by decomposition of hydrocarbons at the surface of white-hot porcelain. Bone and Coward[6] believe that retort carbon is obtained essentially from methane because the carbon produced by cracking methane differs materially from that formed from the other hydrocarbons. In the early days of the war it was believed that a good adsorbent charcoal was to be obtained only by the decomposition of certain hydrocarbons; but that view did not last long. The work of Chaney of the National Carbon Company has thrown some light on portions of this field. Carbon obtained at low temperatures is adsorbent. If formed above 600° it is what Chaney calls gas-treated and is not adsorbent. The higher the temperature, the more the deposit is like graphite. Bone and Coward are wrong in thinking that carbon from methane is necessarily characteristic. The difference is due to the fact that a higher temperature is necessary. While it is of course possible that carbon from different hydrocarbons may be different apart from temperature conditions, there is nothing at present to show this.

Becker[7] claims that when vapors condense to solids, they pass direct to that form without any intermediate formation of liquid. Of course this cannot always be true and can only apply to the particular cases and conditions under consideration by Becker.

[1] Jour. Chem. Soc., **27,** 674 (1874).
[2] Ibid., **60,** 265 (1891).
[3] Comptes rendus, **137,** 706 (1903).
[4] Jour. Soc. Chem. Ind., **12,** 433 (1893).
[5] Jour. Chem. Soc., **62,** 565 (1892).
[6] Ibid., **93,** 1211 (1908).
[7] Zeit. phys. Chem., **78,** 39 (1912).

Dewar[1] states that if a glass rod is cooled to the temperature of liquid air and is then brought into the air of the room, moisture will condense on it as a sheet of ice. If the glass rod is electrified by contact with a piece of silk, the ice forms as a forest of crystals and not as a sheet. The reason for this seems to be that the ice particles are themselves electrified and consequently precipitate as far from each other as possible.

Platinum mirrors were obtained by Wright[2] by electrical disintegration of platinum wires and by Edison[3] by volatilization of electrically heated platinum in hydrogen. Cottrell[4] modified the method of electrical disintegration so as to obtain platinum black.

Any study of the form in which solids precipitate should extend to precipitation from solution, etc., and should include a study of the theory of the formation of mirrors,[5] of the way in which silver precipitates,[6] of mossy copper,[7] of filamentous potassium chloride,[8] of silver chloride growths with silver, sodium chloride, and gelatine,[9] etc.

One particular case of precipitation is so puzzling as to call for special mention. If hydrogen is passed into a saturated aqueous solution of silver oxide containing an excess of the solid salt, silver precipitates to some extent as crystals and in part as colloidal silver.[10] The form in which the metal comes down depends on the nature of the containing vessel. In a platinum vessel no hydrosol is formed and all the silver precipitates in a crystalline form on the walls of the vessel. In vessels of quartz and of ordinary glass, the colloidal silver is yellowish-brown by transmitted light, while it comes down red to blue in a flask made of Jena glass. The ratio of silver hydrosol to ordinary silver is

[1] Chem. News, **97,** 5 (1908).

[2] Am. Jour. Sci. (3) **14,** 169 (1877).

[3] Chem. News, **40,** 152 (1879).

[4] Zeit. phys. Chem., **42,** 385 (1903).

[5] Cf. Wadsworth: Zeit. Instrumentenkunde, **15,** 22 (1895); Neogi: Zeit. anorg. Chem., **59,** 213 (1906); Chattaway: Proc. Roy. Soc., **80A,** 88 (1908).

[6] Cf. Kohlschütter: Zeit. Elektrochemie, **14,** 49 (1908); **18,** 373, 419 (1912); Liebig's Ann., **387,** 86; **309,** 340 (1912); **398,** 47 (1913); Phillips: Jour. Chem. Soc., **72** II, 32 (1897).

[7] Hutchings: Jour. Chem. Soc., **32,** 113 (1877).

[8] Warington: Jour. Chem. Soc., **8,** 30 (1856).

[9] Lüppo-Cramer: Zeit. Kolloidchemie, **9,** 116 (1911).

[10] Kohlschütter: Zeit. Elektrochemie, **14,** 49 (1908).

greater in the Jena glass vessel than in the other two. At first sight one would expect this difference in behavior to be due to differences in material dissolved from the walls; but this is not the case. Kohlschütter allowed water to stand in an ordinary glass flask for a while and then poured it into the Jena glass flask. The reduction product was red. When water which had stood in a Jena glass flask was poured into an ordinary flask or into a quartz one, the silver came down yellowish-brown. The phenomenon is therefore connected with the presence and nature of the solid. The most plausible explanation is, as suggested by Kohlschütter, that the reaction concentrations are highest at the surface of the platinum and lowest at the surface of quartz and the ordinary glass, so that the silver comes down coarsest and most crystalline in platinum vessels and finest in quartz. This could be checked experimentally by determining the adsorbing power of platinum, quartz, and Jena glass for silver oxide and for colloidal silver. It is probable that the adsorption is greatest with platinum and least with quartz. This behavior of the silver may be connected with the fact that it is easier to get a yellow stain[1] of silver on a potash-lime glass than on the hard glasses.

Bredig[2] made use of the arc under water between wire terminals to give him colloidal solutions of platinum and other metals. Schoop[3] has developed a process for plating metals on all sorts of materials by blowing compressed air at about five atmospheres pressure through a pointed nozzle into an arc playing between two wire terminals. Smoo h well-adhering deposits of sprayed metal are obtained when aluminum or copper is sprayed on glass in this way, and the metal adheres so tenaciously that it is impossible to remove the film without destroying the glass surface. It is claimed that a microscopic examination showed that the surface of the glass melts and that the metal is practically fused into the glass. This will happen only when the object to be coated is placed very close to the arc. By working at a longer range it is possible to coat combustible materials like paper and celluloid. It is possible to obtain deposits of brass by making one pole of copper and the other of zinc.

[1] Rosenhain: Glass Manufacture, 185 (1908).

[2] Zeit. Elektrochemie, **4,** 514 (1898); Zeit. phys. Chem., **31,** 258 (1899).

[3] Chem. Abs., **13,** 2640 (1919).

CHAPTER XII

GASES AND SOLIDS IN SOLIDS

Gases in Solids

Reusch[1] points out that the volcanic ash erupted from a volcano often consists of an obsidian glass filled with innumerable gas bubbles and that consequently large pieces will float on water. If the expansion of the gases is too great a glass foam may be obtained which may break down into fragments of glass. Hannay[2] exposed glass at 200° to oxygen and to carbon dioxide at 200 atmospheres pressure, and allowed the glass to cool under pressure. So much gas was taken up that when the glass was heated quickly it passed into a foam. It would probably have been possible to have regulated the pressure and the rate of heating so as to have obtained small but visible bubbles in the glass. In fact this has been done by others when making artificial pumice.[3] As has been pointed out previously, it is very probable that the blue color of many feathers is due to the presence of minute bubbles in the horny part of the feather.[4] When these are seen against a dark back-ground we get a blue analogous to the blue of the sky, due to suspended particles in a homogeneous medium. In the case of the sky the particles are solids or liquids suspended in a gas. In the case of the feathers, we have air bubbles in a solid medium.

The floating soaps contain injected air bubbles and are therefore suspensions of gas in a solid. Bread may also be included under this head. On the other hand a porous plate is really an interlacing system because the gas phase is, or should be, continuous. Porous silica gels occur as opals, as hydrophane, and tabaschir, this last being found in bamboos. In so far as they

[1] Jour. Chem. Soc., **46,** 415 (1884).
[2] Proc. Roy. Soc., **32,** 407 (1881).
[3] Jour. Franklin Inst., **174,** 344 (1912).
[4] Haecker: Zool. Jahrbücher Abt. syst. Geog. Biol. Tiere, **15,** 267 (1920).

are porous they are also interlacing systems. Meerschaum is a silicate mineral coming under the same head.

A special case of gases and solids is a laminated system. Strictly speaking, the gas phase is continuous; but one cannot treat it as a case of a solid dispersed in a gas. Since the air film is very thin, it seems better to consider the theory of lamination here rather than elsewhere. This has been discussed in detail by Tyndall[1] who showed that a laminated structure is produced if an apparently homogeneous mass is subjected to pressure under such conditions that it can yield at right angles to the pressure.[2] He illustrated this by experiments on a mass of pure white wax. When chilled and compressed, it could then be split into laminæ of extraordinary thinness. The same phenomenon occurs on a large scale in nature with many slates. Tyndall points out that we do the same thing in the kitchen when making puff-paste. "The cleavage of our hills is accidental cleavage, but this is cleavage with intention. The volition of the pastry cook has entered into its formation. It has been his aim to preserve a series of surfaces of structural weakness, along which the dough divides into layers. Puff-paste in preparation must not be handled too much; it ought, moreover, to be rolled on a cold slab to prevent the butter from melting and diffusing itself, thus rendering the paste more homogeneous and less liable to split. Puff-paste is, then, simply an exaggerated case of slaty cleavage."

Solids in Solids

Adsorption of a solid by a solid is not properly to be considered as a case of a solid dispersed in a solid because the adsorption is a surface phenomenon. Consequently such things as the pigment lakes are excluded, though it is possible that after ignition they change their type. On the other hand the ultra-microscope shows the presence of a second phase in the case of ruby glass colored by gold. The ruby glass has some very interesting properties.[3] Fused glass containing a small amount of gold is colorless and remains colorless if cooled quickly. If cooled slowly or

[1] Fragments of Science: On Crystalline and Slaty Cleavage.

[2] See, however, Becker: Bull. U. S. Geol. Survey No. 241 (1904); Leith; Ibid. No. 239 (1905).

[3] Zsigmondy: Colloids and the Ultra-microscope, 165 (1909).

if re-heated to a temperature well below the melting-point, it becomes red owing to the separation of particles of gold of the size to transmit red light. If held too long at a high temperature the red color changes to a violet and then to a blue. The changes are exactly those which we get in aqueous solutions and for the same reason, the increase in the size of the particles. It is not quite clear, however, why the chilled glass should be colorless. This cannot be due to the formation of a gold salt because the same phenomenon is observed in a reducing atmosphere. It must either be that the gold is in true solution in the glass or that it has been so peptized by the glass that the colloidal particles are too small to have any effect upon the beam of light. Zsigmondy believes that both things occur though he assumes without any apparently adequate reason that most of the gold is in true solution. It would probably be easy to settle this definitely if experiments were made with a glass richer in gold. With stannic oxide in the glass there is less tendency for he gold to turn blue on prolonged heating and it is therefore easier to match colors.[1] The tinctorial power of the gold is very high, 0.01 percent giving a pink color and 0.1 percent a red. The number of colloidal particles is enormous, billions per cubic millimeter according to Zsigmondy.

The cheaper form of ruby glass owes its color to colloidal copper[2] and the red in some glazes is due to copper in some form. The Chinese ox-blood is believed by Lauth and Dutailly to be metallic copper adsorbed by tin oxide. On rapid cooling a colorless glaze is produced, which turns red on slow heating. Seger[3] does not agree with the view that the red color is due to a segregation of metallic copper. His experiments showed that alternately reducing and oxidizing conditions of the fire gases are necessary to produce the red color. He considers that the color is due to cuprous oxide or cuprous silicate. This opinion is also shared by Stokes[4] who believes that the color transmitted by colloidal copper is blue, whereas this is the color of the coarser colloidal copper.

[1] Bellamy: Jour. Am. Ceramic Soc., **2,** 313 (1919).
[2] Williams: Trans. Am. Ceramic Soc., **16,** 284 (1914).
[3] Collected Writings, **2,** 734 (1902).
[4] Mathematical and Physical Papers, **4,** 245 (1904).

Rosenhain[1] seems to be quite uncertain whether the color of a copper ruby glass is due to metallic copper or to cuprous oxide. In Aventurine glass, the second phase comes out in spangles, presumably of metallic copper. Zulkowski[2] believes that copper ruby glass owes its color to cuprous oxide but the general opinion is against him, though the evidence is not very conclusive.[3] The truth of the matter probably is that we may have metallic copper in one glass and cuprous oxide in another. At present there is no method of differentiating these two cases. On the other hand, it ought to be a simple matter to tell whether one were dealing with cuprous oxide or cuprous silicate because a cuprous silicate glass should be optically empty whereas a cuprous oxide glass should scatter light. It is not easy to see why a cuprous silicate glass should become colorless when fused. Berry[4] describes a red slag from a copper refinery which contained some metallic copper, though not much. When treated with acids about 27 percent Cu_2O dissolved, leaving a pale yellow slag containing 8.6 percent Cu_2O, 11.7 percent FeO, and 49.3 percent SiO_2, the percentages referring to the original composition. Berry considers that the pale yellow is the resultant of green due to the iron and red due to the silver.

Silver yields a beautiful yellow color[5] when applied to glass as a surface stain. This is the color of colloidal silver solutions having the finest particles. The best yellow stain is obtained with potash-lime glasses as the silver tends to come down metallic on the hard glasses. In the case of enamels, silver is added to the mass of the glaze[6] and not as a surface stain. Addition of silver carbonate together with bismuth oxide gives rise to an intense blue. One function of the bismuth oxide is to hold the silver to the body; but it must also cause a partial agglomeration of the silver because the lustres are blue to green instead of yellow to brown. A yellow stain of silver on a cobalt blue enamel gives a green. This is a ceramic analogue of the tree frog.

[1] Glass Manufacture, 182, 184 (1908).
[2] Jour. Soc. Chem. Ind., **16,** 441 (1897).
[3] Thorpe: Dictionary of Applied Chemistry, **2,** 721 (1918).
[4] Am. Chem. Jour., **8,** 429 (1887).
[5] Rosenhain: Glass Manufacture, 185 (1908).
[6] Franchet: Ann. Chim. Phys. (8) **9,** 37 (1906).

Platinum and iridium oxide can be used to give grays, especially in enamels, but they are expensive. Glass can be colored yellow by suspended carbon, the color of thin films of so-called carbon being yellow. Carbon cannot be used in lead glasses because of its reducing action.

Glasses containing no heavy metals are colored yellow to yellowish brown by sulphur; but this is apparently due to formation of polysulphides because these glasses are optically empty.[1] In calcium glasses addition of sulphur gives a blue color, apparently due to the presence of colloidal sulphur. We do not know at all why colloidal sulphur should ever be blue but apparently it may be. Wolfgang Ostwald[2] states that blue and green colloidal solutions of sulphur can be obtained by introducing sulphur into molten sodium chloride, into a borax bead, into liquid ammonia or into hot organic liquids like glycerine. He considers that this blue colloidal sulphur is the cause of the blue color of ultramarine.[3]

In strongly alkaline glasses selenium gives a chestnut brown color and the glasses are then optically empty.[4] In moderately alkaline glasses the color is red to pink and submicrons can be seen. Potash glasses give a purer red than soda glasses. If the red glasses are heated to 620°, the color becomes a pale brownish yellow. Sodium borate glasses containing selenium are often yellow, but turn red when annealed. Colloidal selenium solutions can easily be prepared which are red by transmitted light,[5] almost exactly the color of arterial blood.

In low concentrations tellurium colors glass coral to purple-red and in higher concentrations a steel blue. It is possible to make a blue colloidal solution of tellurium by reducing a dilute boiling mixture of sodium tellurate and sodium protalbinate with aqueous hydroxylamine hydrochloride. It would probably be easy to make a coral-red solution of colloidal tellurium though this appears never to have been done.[6]

[1] Fenaroli: Zeit. Kolloidchemie, **16,** 53 (1915).
[2] Theoretical and Applied Colloid Chemistry, 187 (1917).
[3] See also Morgan: Jour. Oil and Colour Chemists' Ass., **2,** 120 (1919).
[4] Fenaroli: Zeit. kolloidchemie, **16,** 53 (1915).
[5] Schulze: Jour. prakt. Chem. (2), **32,** 390 (1885).
[6] Berzelius: Ann. Phys. (2) **32,** 1 (1834).

Enamels[1] are "vitreous compositions capable of adhering by fusion to the surface of metal or of pottery. The base of the enamel is generally a colorless glass in which are suspended particles of an opaque metallic oxide or salt, generally stannic oxide. Up to about 900° tin dioxide exists finely suspended in the enamel, but ta a higher temperature combination or solution may occur and opacity is diminished. Titanic oxide has been used in place of stannic oxide, and antimony compounds have been employed. Opacity may also be obtained by the use of arsenious oxide, calcium phosphate, cryolite, or fluorspar. A preparation known as artificial cryolite sometimes replaces the mineral. When bone-ash is used, a little nitre may be added to remove the color."

The opacity produced by these added white compounds is due to the difference in refractive index. Natural tin oxide, for instance, has a much higher refractive index for yellow light than glass. While titania has been used as a substitute for stannic oxide, it is not a very good one because it gives a yellow tint. Haber[2] states that six million kilos of stannic acid a year were used for enamelling iron and that this amount was halved when people stopped mixing and melting the oxide with the other constituents of the glaze and merely added it to the enamel just before baking. In the old process a great deal of the stannic oxide was actually dissolved in the glass and consequently did not increase the opacity. Impure zirconia is now being used as a substitute for tin oxide in producing opacity. If the zirconia goes into solution as oxide or as silicate, it does not cause opacity.[3] Of five crystalline titania glazes which were examined,[4] four contained rutile and one probably asgenite. Almost all the titania had crystallized. In a crystalline zinc glaze the crystals resembled willemite. An opaque yellow lead glass is obtained with antimony oxide, the second phase being apparently lead antimoniate, sometimes called Naples Yellow. The black lustre of the Greek and Roman pottery has been reproduced[5] in an

[1] THORPE: Dictionary of Applied Chemistry, **2,** 333 (1918).
[2] Jour. Soc. Chem. Ind., **33,** 49 (1914).
[3] GRUNWALD: Jour. Soc. Chem. Ind., **30,** 210 (1911).
[4] ENDELL: Jour, Soc. Chem. Ind., **30,** 210, 489 (1911).
[5] FRANCHET: Comptes rendus, **152,** 1097 (1911).

oxidizing fire at 850° by fluxing 55 parts of quartz sand with 45 of sodium carbonate and grinding the frit with an equal weight of magnetite. Artificial ferroso-ferric oxide does not yield the black color which is probably enhanced by traces of manganese in the natural ore. The opacity of the enamel is caused by the presence of more stain than will dissolve in the flux. Franchet states that the black enamel was known to the Egyptians and consequently was not discovered by the Greeks. Foster[1] considers that ferrous iron, presumably as ferrous silicate, is the cause of the black color; but Franchet's experiments seem pretty conclusive.

Many of the natural obsidians[2] which appear black consist of a colorless matrix swarming with specks of magnetite. If there is complete oxidation to ferric oxide the color is red. Carnelian is chalcedony containing globules of hematite. If the amount of dispersed material is sufficient to make the mass opaque, we have jasper,[3] which is red with hematite, yellow with limonite and green with saponite or chlorite. Jasper may contain up to twenty percent suspended material.

Blue quartz is not uncommon in the Southern Appalachians and the color is apparently due to the presence of hair-like inclusions of rutile.[4] Since the index of refraction of rutile is very different from that of quartz, this is apparently similar to blue feathers, except that we have here solid particles instead of minute bubbles. Iddings[5] states that the blue color of the opalescent quartz from Llano County, Texas, "is undoubtedly due to reflection of blue light from the minute colorless prisms whose width is a fraction of the length of light waves."

Egyptian blue[6] is crystallized $CaO.CuO.4SiO_2$. It is formed between 800° and 900°, above 900° a green glass being obtained. The reaction is reversible, for blue crystals are formed if the green glass is held at 850°.

Glass can be colored yellow with colloidal cadmium sulphide

[1] Jour. Am. Chem. Soc., **32,** 1259 (1910).
[2] Pirsson: Am. Jour. Sci. (4) **30,** 104 (1910).
[3] Goodchild: Precious Stones, 174 (1908).
[4] Watson and Beard: Proc. Nat. Museum, **53,** 561 (1917).
[5] Jour. Geology, **12,** 227 (1904).
[6] Laurie: Proc. Roy. Soc., **89A,** 418 (1914).

and Horner[1] has produced a yellow of this sort in a boric acid bead. It really would be a good thing if somebody were to take up the whole question of colors in the borax bead so as to determine which were due to colloids and which to true solutions; and also to find out definitely what chemical compounds cause the color in each particular case.

Rock salt has been found having a blue color which is due apparently to colloidal particles of metallic sodium. The same result can be obtained by heating salt with sodium vapor[2] or by exposing salt to cathode rays. Radium emanation colors sodium glasses blue to violet and lead glasses brown.

The action of heat, ultra-violet light, and radium on the colors of gems is very interesting[3] and the theory of it has not been worked out satisfactorily. Pale amethysts become darker when exposed to radium, while ultra-violet light has no effect. When heated to redness in hydrogen or oxygen, the pale amethysts become colorless while they turn yellow if heated in ammonia. The decolorized amethysts regain their color when treated with radium. Rose quartz is made colorless by ultra-violet light and blackish-brown by radium. It is not changed when heated in ammonia. Smoky quartz loses its color when heated and radium brings it back, while hydrogen peroxide tends to make the color yellower. Colorless topaz is made yellow to orange by radium and is decolorized when heated. Ultra-violet light tends to change the orange produced by radium to lilac. Kunzite changes from lilac to green under the influence of radium and is changed back by ultra-violet light. It becomes colorless when heated to 400°; but exposure to radium brings back the blue-green color. Corundum occurs as blue, green, violet, yellow and white sapphires and as ruby. The Oriental sapphire is said by Verneuil[4] to be colored by iron and titanium while the clear sapphire is colored by iron only. Blue sapphires are changed to yellow or yellowish-brown by radium, the blue-green sapphires to green and the white sapphires to yellow. Violet sapphires become pure red and natural rubies lose any violet

[1] Chem. News, **29,** 66 (1874).
[2] Siedentopf: Verh. deutsch. phys. Ges., **7,** 268 (1905).
[3] Doelter: Das Radium und die Farben (1910).
[4] Comptes rendus, **151,** 1053 (1910).

tinge. Artificial rubies and sapphires are no tchanged by exposure to radium, but their coloring matter is chromium or cobalt. Ultra-violet light makes yellow sapphires blue and violet ones more violet. Heating sapphires in air makes htem colorless.

The general result seems to be in all cases that heating makest he gems more nearly colorless[1] and that the action of radium and of ultra-violet light is antagonistic. The only possible explanation seems to be that radium increases the dispersity of the colloidal particles while ultra-violet light decreases it or vice-versa. We know that β rays increase the agglomeration of sulphur and that they change a selenium hyrosol into crystalline selenium. It should be possible to test this explanation on synthetic materials, using perhaps borate glasses. For instance, radium produces no change in pure chromic oxide but turns it brown when the chromic oxide is dissolved in borax. Ultra-violet light changes the brown to yellow and when a chromium oxide borax glass is heated in ammonia it becomes pale. Alumina is not changed by radium but hydrous aluminum oxide sol is turned blue by it. If cases of this sort should be studied carefully it would probably give us the necessary data to straighten out the question of the colors of gems without any difficulty. It is to be noticed that copper oxide adsorbed by alumina is apparently blue,[2] and it is quite possible that magnetite may be.

The presence of surfaces of discontinuity may give rise to color effects without any pigment being present. In mother-of-pearl we have alternate layers of calcium carbonate and of organic matter called conchiolin.[3] On the outside each layer projects slightly beyond the edge of the preceding so that the outside of the nacreous portion shows innumerable steps or ridges running parallel to the growing edge of the shell, thus producing the effect of a diffraction grating. The color of mother-of-pearl is due to the diffraction of light from this grating-like structure and to the interference of light by reflection from numerous parallel laminæ of sensibly equal thickness.

Some crystals of potassium chlorate show brilliant colors and

[1] Cf. Hamlin: The Tourmaline, 87 (1873).

[2] Schenck: Jour. Phys. Chem., **23,** 283 (1919).

[3] Pfund: Jour. Franklin Inst., **183,** 453 (1917); Schade: Kolloidchemische Beihefte, **1,** 385 (1910).

this was found by Stokes to be due to the existence of planes within the crystals at which a periodic twinning had occurred and where there was probably a surface of discontinuity.[1] The same phenomenon is shown by the opal though it is not crystalline. Lord Rayleigh[2] assumes that the reflection takes place at a number of thin laminæ sensibly equidistant, the distance between any two being of the order of magnitude of the light-wave. Crookes[3] says: "When a good fiery opal is examined in daylight, sunlight or artificial light, it appears to emit vivid flashes of crimson, green, or blue light, according to the angle at which the incident light falls, and the relative position of the opal and the observer; for the direction of the path of the emitted beam bears no uniform proportion to the angle of the incident light. Examined more closely, the flashes of light are seen to proceed from planes or surfaces of irregular dimensions inside the stone, at different depths from the surface and at all angles to each other. Occasionally a plane emitting light of one color overlaps a plane emitting light of another color, the two colors becoming visible alternately upon slight variations of the angle of the stone; and sometimes a plane will be observed which emits crimson light at one end, changing to orange, yellow, green, etc. until the other end of the plane shines with a blue light, the whole forming a wonderfully beautiful solar spectrum in miniature. I need scarcely say that the colors are not due to the presence of any pigment but are interference colors caused by minute striæ or fissures lying in different planes."

[1] Wood: Physical Optics, 161 (1911).
[2] Phil. Mag., (5) **26**, 256 (1888).
[3] Proc. Roy. Soc., **17**, 448 (1869).

CHAPTER XIII

THICKNESS OF SURFACE FILMS

The preceding chapters have brought out the importance of films in colloid chemistry and it will perhaps be worth while to get some definite idea of the thickness of the films[1] with which we have been dealing. Oberbeck[2] made experiments to determine what thickness of metal deposited electrolytically on platinum gave the same electromotive force as the massive metal. He found values of 2–3$\mu\mu$ for zinc, 1–2$\mu\mu$ for cadmium, and 1$\mu\mu$ for copper. Since the metal was probably porous and was not burnished, these figures are too high rather than too low. It is interesting to note that the lowest value is obtained with copper, the metal which gives the smallest crystals of the three. Pring[3] determined the minimum thickness of metal which would give the maximum over-voltage. His values vary enormously, being 40$\mu\mu$ for platinum, 5.5μ for zinc, 34$\mu\mu$ for copper, 0.16 mm for nickel, and 6.6 mm for lead. Vincent[4] determined the resistance of thin layers of silver precipitated chemically on glass and found that the specific conductance decreased rapidly after the film became less than 50$\mu\mu$ in thickness. These figures are not very significant because Grimm[5] has shown that the resistance decreases with time and also with pressure. The metal firts precipitated is colloidal silver to some extent and this naturally throws the results out.

Patterson[6] did similar experiments with platinum films produced in a vacuum by cathodic disintegration and obtained constant values for a thickness of 7$\mu\mu$. These values could probably have been decreased considerably by burnishing the platinum.

[1] Freundlich: Kapillarchemie, 265 (1909).
[2] Wied. Ann., **31,** 337 (1887).
[3] Zeit. Elektrochemie, **19,** 255 (1913).
[4] Ann. Chim. Phys. (7) **19,** 421 (1900).
[5] Drude's Ann., **5,** 448 (1901).
[6] Phil. Mag. (6) **4,** 652 (1902).

Wiener[1] prepared thin silver mirrors and determined the change in phase when light was reflected from the two surfaces. The change of phase was constant after a thickness of $12\mu\mu$ was reached, so this is the point at which a silver film behaves like massive metal under these conditions of test. The smallest thickness of metal which could be detected optically by this method was $0.2\mu\mu$. Königsberger and Bender[2] found values of about $50\mu\mu$ for gold and platinum. The least thickness of lead peroxide which can be detected on platinum by optical methods is $0.84\mu\mu$.

Bredig and Weinmayr[3] found that a film of mercury thinner than $0.3–1.5\mu\mu$ would not cause the catalytic decomposition of hydrogen peroxide. Devaux[4] determined the smallest thickness of albumin film which could be considered as solid and obtained values between 0.4 and $8\mu\mu$. Metcalf[5] found about $3\mu\mu$ as the corresponding value for peptone films. Unfortunately he gives no data as to the maximum thickness of peptone films which can be obtained with a peptone solution and yet this is rather an important matter. If the film goes on growing in thickness until practically all the peptone is in the surface, the liquid-vapor interface cannot be important except perhaps just at the start. If the film stops growing in thickness while there is still peptone dispersed through the solution, what is the deciding factor? Shorter[6] has made some experiments on the thickness of saponin films but he does not give any actual thicknesses, merely saying that they are 10–15 molecules thick.

Nagel[7] shows that solid surface films are formed on solutions of $NiCl_2$, $Ni(NO_3)_2$, $CoCl_2$, $CoSO_4$, $FeCl_3$, $FeSO_4$, $K_4Fe(CN)_6$, $MnSO_4$, $MnCl_2$, $Pb(NO_3)_2$, $AgNO_3$, and $KMnO_4$ when the water contains traces of ammonium carbonate, as is usually the case. The thinnest film which he recognized with a cobalt salt had a thickness of about $12\mu\mu$. In many cases the film was $55–270\mu\mu$ in thickness. With colloidal silver a film at least $300\mu\mu$ in thickness was formed. When metals are polished, the surface becomes

[1] Wied. Ann., **31,** 629 (1887).
[2] Drude's Ann., **26,** 763 (1908).
[3] Boltzmann Festschrift, 839 (1904).
[4] Jour. Phys. (4) **3,** 450 (1904).
[5] Zeit. phys. Chem., **52,** 1 (1905).
[6] Phil. Mag. (6), **17,** 560 (1909).
[7] Drude's Ann., **29,** 1029 (1909).

more finely crystalline and thus constitutes a film which differs from the mass of the metal.[1] In the more easily flowed metals the surface films formed by polishing them may vary from 1–5μ in thickness, while in the less easily flowed metals they may be 0.5μ or less. At surfaces which have moved over each other very slightly, films of only a comparatively few molecules in thickness might be formed.

Bodenstein and Fink[2] estimated the thickness of the adsorbed film of sulphur trioxide on platinum at 248° as 1.2$\mu\mu$ on the explicit assumption that the density of the film was 2. Gurwitsch[3] considers that the thickness of the adsorbed liquid on silver foil is 35, 33 and 28$\mu\mu$ for carbon tetrachloride, carbon bisulphide and acetone respectively.

Ihmori[4] determined the amount of moisture on different surfaces gravimetrically and estimated the thickness of the water film to be 3–10$\mu\mu$ on metals and 22$\mu\mu$ on quartz. Langmuir[5] questions the accuracy of these results. Ihmori found no measurable adsorption with polished or ignited platinum. With the other metals the amount of apparently adsorbed moisture became quite appreciable if the metal were allowed to stand in the air for a few weeks and Ihmori states expressly that the small amount of water adsorbed by the polished metals is perhaps due to the presence of a thin film of oxide. If the film of oxide is porous, as it probably would be, its surface is vastly different from that postulated by Ihmori in his calculations. Langmuir points out that with glass there is evidence that water may penetrate quite a way. If a 40 watt incandescent lamp bulb, which has been exhausted and dried at room temperature, is heated to 500° for several hours, it loses enough gas to form a layer of water 55 molecules deep (0.00225cc/cm^2) of carbon dioxide 4.8 molecules deep (0.00015 cc/cm^2); and of nitrogen 0.9 molecules deep (0.000015cc/cm^2) all over the surface.[6] Since there cannot possibly have been this amount of gas on the surface of the

[1] Beilby: Phil. Mag. (6) **8,** 258 (1904).
[2] Zeit. phys. Chem., **60,** 1 (1907).
[3] Jour. Russ. Phys. Chem. Soc., **47,** 805 (1915).
[4] Wied. Ann., **31,** 1006 (1887).
[5] Jour. Am. Chem. Soc., **38,** 2284 (1916).
[6] Langmuir: Trans. Am. Inst. Electr. Eng., **32,** 1921 (1913).

bulb, most of it must have come from the mass of the glass. Katz[1] found that, with 70 percent humidity, powdered quartz takes up 1.3×10^{-3} mg of water and anorthite 6.2×10^{-3} mg per square centimeter. This corresponds to layers of water 43 and 205 molecules deep respectively. Langmuir believes that there either was penetration of water into the solids or that Katz was measuring moisture condensed as liquid in the capillary spaces between the fine grains. Sherwood[2] finds that glass which has been annealed above 200° adsorbs gases to give a layer about one molecule thick.

From their experiments on the heats of adsorption of vapors by charcoal, Lamb and Coolidge[3] conclude that the adsorbed liquids are present in films many molecules deep. With carbon bisulphide the thickness of the layer was forty molecules, assuming $0.1\mu\mu$ as the thickness of a molecular layer. In the experiments with ethyl alcohol, the same calculation gives a layer about one molecule thick.

Pettijohn[4] found about $128\mu\mu$ for the maximum thickness of a water film on some glass pearls made in Germany. With another lot of glass of different origin the corresponding value was about $68\mu\mu$. With river sand the estimated thickness of the film varied from $285\mu\mu$ with 10-mesh sand to $114\mu\mu$ with 60-mesh sand. Experiments with nitrobenzene, aniline, dimethylaniline, phenyl iodide, toluene, turpentine, and pyridine indicated that the thickess of the film is independent of the liquid used, a result which can hardly be strictly true.

Parks[5] finds that when glass wool at 12° has a surface film of water $134\mu\mu$ in thickness, further addition of water causes no evolution of heat. From data by Barus[6] on the formation of fog he calculates that, under the conditions of the experiments, the thickness of the water film is 0.1–0.8μ when the nucleus has a diameter of 2.6μ and is 0.05–0.5μ when the nucleus has a diameter of 3.6μ. According to J. J. Thomson[7] the mean radius of

[1] Proc. Amsterdam Acad., **15,** 445 (1912).
[2] Jour. Am. Chem. Soc., **40,** 1645; Phys. Rev. (2) **12,** 448 (1918).
[3] Jour. Am. Chem. Soc. **42,** 1168 (1920).
[4] Ibid., **41,** 477 (1919).
[5] Phil. Mag. (6) **5,** 517 (1903).
[6] Ibid. (6) **4,** 24, 262 (1902).
[7] The Discharge of Electricity through Gases (1900).

drops formed on negatively electrified oxygen is about 0.8μ and on positively electrified oxygen is about 0.7μ.

Sohncke[1] believed that films of oil on water were instable when less than 100$\mu\mu$ in thickness. This does not mean that thinner films cannot be obtained; but merely that this thickness is necessary to give a stable film having the properties of oil in mass. Fischer[2] worked with films of oil on mercury less than 5$\mu\mu$ in thickness; but these do break up into drops in time. Lord Rayleigh[3] found that a layer of oil 1$\mu\mu$ in thickness causes a perceptible change in the surface tension of water and that a layer of 1.6$\mu\mu$ in thickness contaminates the water sufficiently to affect the motion of a piece of camphor over it. Even with a layer of castor oil 8$\mu\mu$ in thickness, the surface tension was still dropping. Langmuir[4] considers that when a drop of oil is allowed to spread over a large surface of water, it will do so until the layer is one molecule thick. This is very possibly true; but Langmuir gives himself a certain amount of leeway because he admits the possibility of the molecules of oil being packed on the surface in different ways. He is not interested at all in the maximum thickness of the film.

Hatschek[5] estimates the thickness of the adsorbed water film on particles of colloidal sulphur at 0.87$\mu\mu$. In the case of cataphoresis, Cotton and Mouton[6] believe that the effect of the walls is manifest to a distance of 25$\mu\mu$.

The black film in a soap-bubble is apparently about 17$\mu\mu$ in thickness[7] when there is no sodium nitrate in solution and about 12$\mu\mu$ in thickness[8] when there is. If this difference is real it is because the film is less hydrous in presence of sodium nitrate. At higher temperatures the thickness[9] may drop to 5$\mu\mu$. I have not been able to find any statement as to the maximum thickness of a soap-bubble film; but it is certainly not less than 1.4μ.

[1] Wied. Ann., **40,** 345 (1890).
[2] Ibid., **68,** 414 (1899).
[3] Phil. Mag. (5) **48,** 331 (1899).
[4] Jour. Am. Chem. Soc., **39,** 1848 (1917).
[5] Zeit. Kolloidchemie, **11,** 280 (1912).
[6] Nordenson: Kolloidchemische Beihefte, **7,** 108 (1915).
[7] Drude: Wied. Ann., **43,** 158 (1881).
[8] Reinold and Rücker: Phil. Trans. **174,** 645 (1883).
[9] Johonnot: Phil. Mag. (5) **47,** 501 (1899); (6) **11,** 746 (1906).

When studying reaction velocity in heterogeneous systems, it has been found desirable in many cases to assume the existence of a film of saturated solution in contact with the solid, the rate of reaction depending on the rate of diffusion. The thickness of this film can be varied a great deal by varying the rate of stirring. Under the conditions in which Brunner[1] was working the thickness of these films was 20–50μ.

From this outline, it is evident that the thinnest films which can be detected at present are about 0.2–1.0$\mu\mu$ in thickness, which corresponds fairly well to a layer one molecule thick, although there is no apparent reason why one should not detect a film before it covers the surface completely and it is probable that one does in a good many cases. The thickness at which a film has the properties of matter in mass may vary from 1–3$\mu\mu$ in the case of metals, up to much higher values in the case of oils. The maximum thickness to which films can grow and still be classed as films has not been determined in any case, except perhaps for the metals; but it may very likely run up to 100μ in special cases. There are certain matters in regard to the regions of discontinuity in soap-bubble films which call for a good deal more study. Nobody seems to have considered in any suitable way the question of the varying hydrolysis with varying thickness of the film.

Perrin[2] gives the following estimated values in $\mu\mu$ for the diameters of some molecules: helium, 0.17; argon, 0.27; mercury, 0.28; hydrogen, 0.20; oxygen, 0.26; nitrogen, 0.27; chlorine, 0.4; ether 0.6.

[1] Zeit. phys. Chem., **47,** 56 (1904).

[2] Kolloidchemische Beihefte, **1,** 265 (1910).

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